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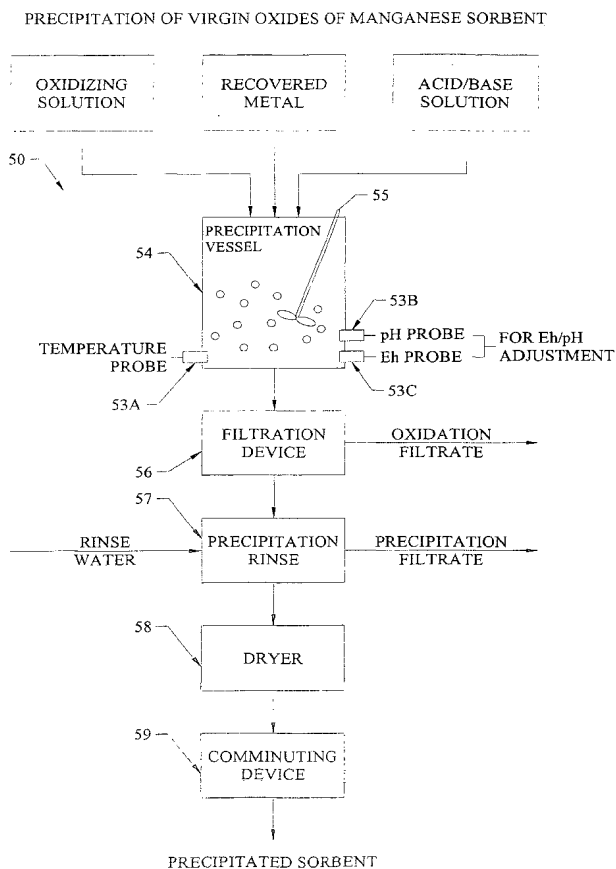A.; 2008 Dixon Drive, Bloomington, MN 55431 (US).

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(54) Title: DISASSOCIATION PROCESSING OF METAL OXIDES

PRECIPITATION OF VIRGIN OXIDES OF MANGANESE SORBENT

(57) Abstract: The invention relates to systems and processes
for recovery and/or extraction of metal values from ore or other
raw material containing oxides of the metal and to precipita-
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lutant loading capacities equal to or greater than that of the
metal oxides in the ore or other raw material which are suit-
able, amongst other uses, as a sorbent for capture and removal
of target pollutants from industrial and other gas streams. Fur-
ther, the invention relates to oxides of metals so recovered and
precipitated.

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DISASSOCIATION PROCESSING OF METAL OXIDES

Related Applications

This application claims priority to U.S. Provisional Application No. 60/387,994, filed June 11, 2002, U.S. Provisional Application No. 60/342,587, filed December 21, 2001, now U.S. Patent Application No. 10/328,490, filed December 23, 2002 and International Application No. US02/41276, filed December 23, 2002, and U.S. Provisional Application No. 60/362,477, filed March 6, 2002, now U.S. Patent Application No. 10/384,473, filed March 6, 2003 and International Application No. US03/07098, filed March 6, 2003, which are incorporated by reference herein.

Field of the Invention

The invention relates to systems and processes for recovery and/or extraction of metal values from ore or other raw material containing oxides of the metal and precipitation of oxides of metals that have oxidation states and/or pollutant loading capacities equal to or greater than that of the metal oxides in the ore or other raw material which are suitable, amongst other uses, as a sorbent for capture and removal of target pollutants from industrial and other gas streams. Further, the invention relates to oxides of metals so recovered and precipitated.

Background of the Invention

Metal oxides of various types have been found to have very beneficial properties. For example, oxides of manganese are utilized for a number of industrial applications, such as pollution control systems, steel manufacture, batteries and catalytic converters, to name a few. Of particular, but not exclusive, interest to Applicants is the use of oxides of manganese in pollution control systems. Applicants are co-inventors of the subject matter of co-pending U.S. patent applications numbers 09/919,600, 09/951,697, 10/044,089 and 10/025,270, the disclosures of which are incorporated herein by reference. These applications disclose pollutant removal systems and processes, known as Pahlman™ systems and processes, which utilize dry and wet removal techniques and combinations thereof, incorporating the use of

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oxides of manganese as a sorbent for capture and removal of target pollutants from gas streams.

Metal oxides that are useful in these applications are not limited to manganese oxides. Any metal oxide that forms soluble and/or thermally decomposable metal salts when reacted

5   with target pollutants in a gas stream may be used in such pollutant removal systems and are relevant to this invention. Suitable metal oxide will react with a target pollutant to produce a reaction product exhibiting one or both properties. Metal oxides that can yield reaction products with the desired properties include, but are not limited to representative metals and transition metals.

10   Before going further, the following definitions will be with respect to this background discussion and to the understanding of the invention disclosed herein:

The term "target pollutant," as used herein, refers to the pollutant or pollutants that are to be captured and removed from a gas stream. Examples of target pollutants that may be removed with an oxide of metal sorbent include, but are not limited to, NOX, SOX, mercury

15   (Hg) and mercury compounds, H2S and other totally reduced sulfides (TRS), chlorides, such as hydrochloric acid (HCl), and oxides of carbon (CO and CO2).

"Reacted" or "loaded," as used interchangeably herein, refers in conjunction with "oxides of metal," "oxides of manganese," and/or "sorbent" to oxides of metal, oxides of manganese, or sorbent that has interacted with one or more target pollutants in a gas whether

20   by chemical reaction, catalysis, adsorption or absorption. The term does not mean that all reactive or active sites of the sorbent have been utilized as all such sites may not actually be utilized.

"Unreacted" or "virgin," as used interchangeably herein, refers in conjunction with "oxides of metal," "oxides of manganese" and/or "sorbent" to oxides of metal, oxides of

25   manganese or sorbent that has not interacted with target pollutants in a gas or gas stream.

"Nitrates of manganese," as used herein, refers to and includes the various forms of manganese nitrate, regardless of chemical formula, that may be formed through the chemical reaction between NOX and the sorbent and includes hydrated forms as well.

"Sulfates of manganese," as used herein, refers to and includes the various forms of

30   manganese sulfate, regardless of chemical formula that may be formed through the chemical reaction between SOX and the sorbent and includes hydrated forms as well.

"Metal oxide stability area" or "stability area," as used herein, refers to the region of thermodynamic stability for metal oxides at their valence states delineated by Eh and pH values for aqueous solutions or, phrased alternatively, the domain of metal oxide stability for an aqueous solution. More specifically, it refers to the region or domain delineated by Eh and pH values for aqueous solutions in an electrochemical stability diagram, such as presented by Pourbaix diagrams and their equivalents, such as the Latimer Diagram or the Frost Diagram.

"MnO_2 stability area," as used herein, refers to the metal oxide stability area for manganese dioxide; or, phrased alternatively, the region or domain of MnO_2 stability delineated by Eh and pH values for aqueous solutions in an electrochemical stability diagram, such as presented by Pourbaix diagrams and their equivalents, such as the Latimer Diagram or the Frost Diagram.

"Recovered metal values" or "recovered manganese values," as used herein, refers to metal or manganese recovered from raw metal ores or nodules or other .

"Regenerated oxides of metal" or "regenerated oxides of manganese," as used herein, refers to loaded or reacted oxides of manganese that have been processed according to the methods of the invention in which a heated aqueous oxidizing solution is mixed with a heated slurry of loaded oxides of metal to form a mixture, or a heated aqueous oxidizing solution to which loaded oxides of metal are added to from a slurry mixture, the mixtures being adjusted and maintained so as to be within the metal oxide stability area.

"Precipitated oxides of metal" or "precipitated oxides of manganese," as used herein, refers to oxides of metal formed or newly formed by precipitation from a mixture of a heated metal salt solution and a heated aqueous oxidizing solution or a mixture formed by addition of manganese salt solution to a heated aqueous oxidizing solution, the mixtures being adjusted and maintained so as to be within the metal oxide stability area.

Oxides of manganese or other metals in various forms, utilized as sorbents, are introduced into the Pahlman™ systems (and other pollution removal systems) and interact with the target pollutants in gas streams routed through the systems as a catalyst, a reactant, an absorbent or an adsorbent. Without being limited and by way of example, in one possible interaction in the process of pollutant removal, the oxidation (or valence) state of the oxides of manganese sorbent, for example, is reduced from its original state during reaction with the

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target pollutants. For example, where the target pollutants are NOX or SO2, pollutant removal occurs possibly through overall reactions such as the following:

$SO_2 + MnO_2 \rightarrow MnSO_4$ Reaction (1)

5       $2NO + O_2 + MnO_2 \rightarrow Mn(NO_3)_2$ Reaction (2)
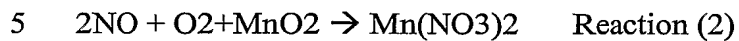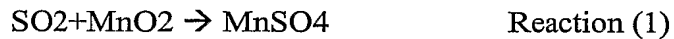
In both of the reactions above, manganese (Mn) is reduced from the +4 valence state to +2 valence state during formation of the reaction products shown. It should be noted that the actual reactions may include other steps not shown, and that indicating Reactions 1 and 2

10   is solely for illustrative purposes.

Many representative and transition metals, and therefore oxides of these metals, may exist in different valence (oxidation) states. Of particular interest and usefulness for gaseous pollutant removal are those oxides of manganese having valence states of +2, +3, and +4, which correspond to the oxides MnO, Mn_2O_3, MnO_2 and Mn_3O_4. The oxide Mn_3O_4 is

15   believed to be a solid-solution of both the +2 and +3 states.

A characteristic of most oxides of manganese species is non-stoichiometry. For example; most MnO_2 species typically contain on average less than the theoretical number of 2 oxygen atoms, with numbers more typically ranging from 1.5 to 2.0. The non-stoichiometry characteristic of oxides of manganese is thought to result from solid-solution

20   mixtures of two or more oxide species (such as may occur in the oxide Mn_3O_4), or distortions of molecular structure and exists in all but the beta (β), or pyrolusite, form of manganese dioxide. Oxides of manganese having the formula MnO_X where X is about 1.5 to about 2.0 are particularly suitable for use as sorbent for dry removal of target pollutants from gas streams and may be also be utilized in wet removal. However, the most active types of

25   oxides of manganese for use as a sorbent for target pollutant removal usually have the formula $MnO1.7$ to 1.95, which translates into average manganese valence states of +3.4 to +3.9, as opposed to the theoretical +4.0 state. It is unusual for average valence states above about 3.9 to exist in most forms of oxides of manganese.

Oxides of manganese are known to exhibit several identifiable crystal structures,

30   which result from different assembly combinations of their basic molecular structural units. These basic structural "building block" units are MnO_6 octahedra, which consist of one manganese atom at the geometric center, and one oxygen atom at each of the six apex positions of an octahedral geometrical shape. The octahedra may be joined together along

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their edges and/or corners, to form "chain" patterns, with void spaces ("tunnels"). Regular (and sometimes irregular) three-dimensional patterns consist of layers of such "chains" and "tunnels" of joined octahedra. These crystalline geometries are identified by characteristic x-ray diffraction (XRD) patterns. Most oxides of manganese are classifiable into one or more

5   of the six fundamental crystal structures, which are called alpha (α), beta (β), gamma (γ), delta (δ), epsilon (ε), and ramsdellite. Certain older literature also included rho (ρ) and lambda (λ) structures, which are now thought obsolete, due partly to improvements in XRD technique. Some (amorphous) forms of $MnO2$ exhibit no crystalline structure. Oxides of other transition metals and some representative metals also may have wide varieties of

10   stoichiometric configurations and crystalline structures similar to the manganese example.

One of the key features of transition metal chemistry is the wide range of oxidation states (oxidation numbers) that the metals can show. Certain characteristics of oxides of metals probably arise from the size and shape of voids within these crystalline patterns and from certain elements, and compounds, which may occupy the voids and appear to help

15   prevent collapse of certain structures. Applicants believe that these characteristics in addition to the oxidation state may have an affect upon the loading capacity of oxides of metal sorbent. Further, many oxides of metals, including those that are the subject of the present, come in hydrated or hydrous forms, having water chemically bound or combined to or within their crystalline structures, containing one or more molecules of water; this is sometimes

20   referred to as bound water, structural water, water of crystallization or water of hydration. In these forms, the water is combined is such a way that it may be removed with sufficient heat without substantially changing the chemical structure of the oxides of metal. Such oxides of metal are also useful as a sorbent. This bound water may also contribute to the chemical reactivity and possibly catalytic behavior of the species.

25   Some oxides of metal have the ability to absorb oxygen from gas. Manganous oxide (MnO) and $Mn(OH)2$ will oxidize to $MnO2$ in the presence of air, for example. Additionally, the dioxides of manganese are themselves oxidizers. They readily exchange oxygen in chemical reactions and are known to have catalytic properties. This oxygen exchange ability may be related to proton mobility and lattice defects common within most $MnO2$ crystal

30   structures.

The oxidizing potential of $MnO2$ and other metal oxides is advantageously utilized in target pollutant removal in the Pahlman™ and other pollutant removals systems and

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processes. Target pollutants, such as NOX, SO2, CO, and CO2 gases, mercury (Hg) and other pollutants, require oxidation of the species prior to reaction with metal oxide sorbent to form reaction products, such as metal sulfates, nitrates, and carbonates, mercury compounds, and other metal salts and corresponding reaction products, in order for them to be captured and removed from gas streams.

Manganese sulfate and nitrate salts are soluble in water, while manganese oxides are not. During the formation of reaction products such as manganese nitrates and sulfates, the manganese present is converted from an insoluble oxide to a soluble metal salt. This property allows the reaction products formed on the surface of oxides of manganese sorbent particles to be readily dissolved and removed from the sorbent particles in aqueous solutions by disassociation into reaction product anions, such as sulfate or, nitrate, and manganese cations such as $Mn+2$ cations. This property may be advantageously utilized with other metal oxide sorbents as well.

Manganese dioxides are divided into three origin-based categories, which are: 1) natural (mineral) manganese dioxide (NMD), 2) chemical manganese dioxide (CMD), and 3) electrolytic manganese dioxide (EMD). As implied, NMD occurs naturally as various minerals, which may be purified by mechanical or chemical means. The most common form of NMD is pyrolusite (β-MnO2), which is inexpensive, but has rather low chemical activity and therefore low pollutant loading capacity. CMD and EMD varieties are synthetic oxides of manganese. EMD is produced primarily for the battery industry, which requires relatively high bulk density (which often results from relatively large, compact particles), relatively high purity, and good electrochemical activity. Though useful as sorbent, characteristics such as low surface area and large compact particle size make EMD somewhat inferior to CMD for gas removal applications, despite its good electrochemical activity. Chemically synthesized oxides of manganese of all kinds fall into the CMD category and includes chemically treated or pretreated oxides of manganese. In chemical synthesis, a great deal of control is possible over physical characteristics such as particle size and shape, porosity, composition, surface area, and bulk density in addition to electrochemical or oxidation potential. It is believed that these characteristics contribute to the loading capacity of some oxides of manganese.

Oxides of manganese and other metals have the ability to capture target pollutants from gas streams, however, the low pollutant loading rates achieved with various prior art oxides of metals have made some industrial applications of this characteristic uneconomical.

The low target pollutant loading rates of various prior art oxides of metal sorbents would require voluminous amounts to effectively capture large quantities of target pollutants that exist at many industrial sites, e.g., NOx and/or SO2. The large quantity of sorbent that would be required to capture NOx and/or SO2 could result in an overly costly pollutant removal

5   system and sorbent regeneration system. It would therefore be desirable to enhance the loading capacities of the oxides of metal sorbents in order to economically implement a pollution removal system utilizing oxides of metals.

Using manganese as an example, it is believed that metal salt reaction products, such as the manganese salts of Reaction (1) and Reaction (2) above, form on the surfaces of the

10   sorbent particles of oxides of manganese. These reactions may extend to some depth inside the sorbent particles and into the pores and micro fissures. Applicants believe that formation of such reactions products occurs primarily on the surfaces of the oxides of manganese particles, resulting in a layer or coating, which effectively isolates the covered portion of the particle surface and thereby prevents continued rapid reaction with additional target

15   pollutants. Further, the oxidation state and thus the loading capacity of the oxides of manganese below the surface of the reaction product coating may be reduced during the pollutant removal, thus diminishing the loading capacity of sorbent even after the reaction product have been removed or disassociated into an aqueous solution. It would therefore be desirable for economic reasons to re-use or regenerate the unreacted portions of the sorbent

20   for subsequent cycles of pollutant gas removal.

In order to regenerate the reacted oxides of manganese effectively for subsequent re-use as a gas sorbent with high removal efficiencies and target pollutant loading rates, it is advantageous to: (1) remove soluble reaction products or reaction product salts, such as salts $MnSO_4$, $Mn(NO_3)_2$, $MnCl_2$ and other manganese halides, manganese salt reaction products,

25   and the like, from the sorbent particle surfaces with an aqueous solution through disassociation into their constituent cations and anions, e.g, Mn^{+2}, Cl^{-1} SO_4^{-2}, and NO_3^{-1} ions; (2) restore or increase the target pollutant loading capacity and/or oxidation state of the remaining solid oxides of manganese sorbent below the surface of the reaction product coating that is now dissociated in an aqueous solution, (3) recover, through precipitation, the

30   Mn^{+2} ions that were dissociated into solution from the reaction products formed through reactions with the various target pollutants; and (4) to recover other ions and form marketable or otherwise useful by-products. Note that some soluble and insoluble reaction products may be removed through thermal decomposition.

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Applicants have developed methods of recovering metal values by converting insoluble metal oxides to soluble metal salts and recovering the solution so formed. For example, ore deposits or extracted ore containing metal of interest may be leached either in situ or after extraction. Applicants can treat this solution of soluble metal salts to produce oxides of metal useful, amongst other applications as sorbent for pollutant removal. Oxides of metal so produced may exhibit high or increased loading capacity and/or valence states as compared to reacted and virgin oxides of metal of various forms, including a variety of commercially available oxides of metal.

One objective of this invention is to create active metal oxides by recovering metal values from ore deposits or extracted ore by converting insoluble metal oxides in the ore to soluble metal salts and pumping the solution so formed out of the ore, either in situ or from ore that has been extracted from the earth, and oxidizing the soluble metal salt through an oxidation process.

Brief Description of the Drawings

Figure 1 is a Pourbaix diagram for an aqueous solution of 1 mole/liter manganese ion concentration.

Figure 2 is a Pourbaix diagram for an aqueous solution of 10-6 mole/liter manganese ion concentration.

Figure 3 is a block flow diagram of a system and process according to the invention.

Figure 4 is a block flow diagram of system and process according to the invention with electronic controls.

Figure 5 is a block flow diagram of system and process according to the invention with electronic controls.

Figure 6 is a block flow diagram of system and process according to the invention with electronic controls.

Figure 7 is a graph plotting SOX loading capacities of oxides of manganese.

Figure 8 is a graph plotting NOX loading capacities of oxides of manganese.

Figure 9 is a graph plotting pH and Eh values relative to processing times.

Figure 10 is a graph plotting pH and Eh values relative to processing times with and without pH control.

Summary of the Invention

The invention relates to systems and processes for recovery and precipitation of oxides of metals that have high oxidation states and/or high pollutant loading capacities which are suitable, amongst other uses, as a sorbent for capture and removal of target pollutants from industrial and other gas streams from ore or other raw material containing impure oxides of the metal.

In an embodiment of a method of the invention ore containing a target metal is processed to recover dissociated metal salts which are precipitated to form oxides of the target metal. The method of this embodiment comprises the steps of: leaching metal values from ore to form a solution containing cations and anions of disassociated metal salts; heating the solution containing cations and anions of disassociated metal salts; mixing the heated solution containing cations and anions of disassociated metal salts and a heated aqueous oxidizing solution in a precipitation vessel to form a solution mixture, the heated aqueous oxidizing solution being prepared so as to have Eh and pH values within the metal oxide stability area of an aqueous solution heated to a temperature at or near boiling temperature at atmospheric pressure and being heated to a temperature at or near the boiling temperature; monitoring and adjusting the temperature, Eh value and pH value of the solution mixture so as to rapidly move mixture conditions into and to maintain them within the metal oxide stability area; and maintaining the solution conditions within the metal oxide stability area so as to precipitate the metal cations out of solution as precipitated oxides of metal having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material.

In another embodiment of a method, ore containing manganese is processed to recover dissociated manganese salts which are precipitated to form oxides of manganese. The method of this embodiment comprise the steps of: leaching manganese values from ore to form a solution containing cations and anions of disassociated manganese salts; heating the solution containing cations and anions of disassociated manganese salts; mixing the heated solution containing cations and anions of disassociated manganese salts and a heated aqueous oxidizing solution in a precipitation vessel to form a solution mixture, the heated aqueous oxidizing solution being prepared so as to have Eh and pH values within the MnO_2 stability area of an aqueous solution heated to a temperature at or near boiling temperature at atmospheric pressure and being heated to a temperature at or near the boiling temperature; monitoring and adjusting the temperature, Eh value and pH value of the solution mixture so as to rapidly move mixture conditions into and to maintain them within the MnO_2 stability

area; and maintaining the solution conditions within the MnO2 stability area so as to precipitate the manganese cations out of solution as precipitated oxides of manganese having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material.

5   Other embodiments of the invention include the oxides of metal produced by the above methods. The above methods may further comprise the step of maintaining solution or solution mixture pH constant throughout the processing cycle.

In any of the above methods, the aqueous oxidizing solution may contain a suitable or compatible oxidant or oxidizer included but not limited to those selected from the group 10 consisting of persulfates, chlorates, perchlorates, permanganates, peroxides, hypochlorites, oxygen, air, and ozone (O3).

In another embodiment of the invention is a system for rapid and adaptive recovery of metal values as precipitates of oxides of metal having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material, the 15 system comprising; a well bore hole for injecting a leaching solution; a well bore hole for recovering a solution containing cations and anions of disassociated metal salts; a precipitation vessel equipped with probes for measuring temperature, Eh and pH values of aqueous solutions within the precipitation vessel, the precipitation vessel being configured for introduction of a solution containing cations and anions of disassociated metal salts; a oxidant 20 feeder containing a supply of aqueous oxidizing solution, the aqueous oxidizing solution being prepared so as to have Eh and pH values within the metal oxide stability area for an aqueous solution heated to a temperature at or near boiling temperature at atmospheric pressure; a heater for providing heat to the precipitation vessel; a base and/or acid feeder for feeding base or acid to the precipitation vessel; a least one filtration and/or rinse unit, which 25 optionally may be incorporated into and a part of the precipitation vessel; and a controller for simultaneously monitoring and adjusting system operational parameters and regulating system components, the controller being in electronic communication with the probes of the precipitation vessel, the feeders, the at least one filtration and/or rinse unit and the heaters; the controller being capable of monitoring and adjusting system operational parameters 30 selected from the group consisting of temperature, Eh, pH and feeder rates so as maintain conditions in the oxidation vessel within the metal oxide stability area through processing cycles.

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Detail Description of Preferred Embodiments

The methods and systems of the invention each involve and employ Applicants' recognition that oxides of metal processed in aqueous systems in which conditions and parameters are adjusted and maintained within the metal oxide stability area will yield oxides

5   of metal having desired pollutant loading capacities and/or oxidation states. In its various embodiments, the invention and the methods and systems thereof provide for rapid, adaptive and stable processing of oxides of metal as compared to the methods and systems currently know in the art. Oxides of metal thus processed are suitable for use as a sorbent in dry and wet gaseous pollutant removal systems and are particularly suitable for use in dry pollutant

10   removal systems. They may also be utilized in a variety of commercial, industrial and other applications, unrelated to pollutant removal, that incorporate or employ oxides of metal.

The metal values used in the invention are recovered from raw in situ ore, recovered ore, or from metal oxides in particle form by a leaching process. Applicants believe that, by way of non-limiting example, some metals so leached occur naturally in an insoluble oxide

15   form which is reduced through the use of a reducing agent, and reacted with an anion to form a soluble metal salt. The anion may be provided by the reducing agent itself or it may be an additional element in the leaching solution. Possible leaching solution active components are water containing dissolved sulfur dioxide, nitric, nitrous, sulfuric, or sulfurous acids, soluble salts of hydrosulfite, bisulfite, or metabisulfite or other chemicals capable of dissolving the

20   metal oxides of interest.

This leaching process can take place in situ, with the metal containing ore or nodule still in the earth or sea bed, or with the ore extracted from the earth previously, or metal oxides in particulate form, such as those that are commercially available. Underground mineral leaching involves injecting a leaching solution into the rock or ore deposit at one

25   point and retrieving it by known leachate extraction techniques such as pumping it out from a lower point after the solution has passed through the rock formation. The leaching solution dissolves some of the metal of interest, which is recovered as a component of the recovered solution. Typically a series of injection and recovery holes are drilled into the formation containing the ore. The leaching solution is then injected into the formation. Natural fissures

30   in the rock formation may allow the leaching solution to sub-optimally pass by some of the mineral bearing ore without penetrating the formation and recovering the mineral. Therefore the pressure of the leaching fluid is kept relatively low to avoid fracturing the rock formation further and increasing this bypass phenomenon.

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The minerals could also be recovered through traditional open-cut or subterranean mining where the mineral bearing rock is brought to the surface. The rock may be crushed and the minerals may then be extracted chemically using similar leaching solutions and producing similar solutions of metal salts.

5   Without being bound by theory or limited by this example, Applicants believe that the processing of recovered metal oxides values, such as manganese cations and the precipitation of newly formed metal oxides, e.g., oxides of manganese in a heated aqueous oxidizing solution system maintained within the metal oxide stability area may beneficially affect a number of characteristics of the metal oxides. Such characteristics include, but are not

10   limited to, particle size and shape, crystalline structure or morphology, porosity, composition, surface area (BET), bulk density, electrochemical or oxidation potential and/or metal valence states. Some or all of these characteristics affect the performance of metal oxides of manganese in their various uses and, particularly, in their use as a sorbent for removal of gaseous pollutants. With attention to maintaining aqueous system conditions within the

15   stability area, Applicants have found that they are able to produce metal oxides, particularly oxides of manganese, having desirable loading capacities and/or metal valence states.

The application of these principles can be understood with reference to the following discussion relative to oxides of manganese. The stability area for an aqueous system will vary based upon the conditions of the system and may shift or drift as reactions in the

20   aqueous system proceed. With oxides of manganese as an example, changes in dissolved manganese ion concentration, oxidizer concentration, pH, Eh, solution temperature, and competing dissolved ions may affect the boundaries of the domain or region of stability for MnO_2. The aqueous oxidizing solution systems of the invention are typically at temperatures at or near the boiling temperature of aqueous solutions at given atmospheric pressures. The

25   boiling point of aqueous solutions will vary depending upon elevation and will be different at sea level than at other elevations. The effects of such changes or different atmospheric conditions upon the boundaries of the MnO_2 stability area or other metal oxide stability area on a Pourbaix Eh-pH diagram can be determined either by empirical data derived from experimentation or with computer software programs known to those skilled in the art, such

30   as HSC Chemistry distributed by Outokumpu Oy of Finland. Software may also be written to determine stability areas as defined by other diagrams, such as the Latimer Diagram or the Frost Diagram.

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With reference to Figures 1 and 2, impact of system conditions on the MnO_2 stability area is illustrated with respect to Pourbaix diagrams for systems at 25° C and at atmospheric pressure at sea level. In Figure 1, the ranges of pH and Eh values for thermodynamically stable aqueous solutions of various manganese compounds are illustrated in graph form for

5   aqueous solution systems at 25° C and a 1mole/liter manganese ion concentration. Figure 2 similarly illustrates ranges of pH and Eh values for aqueous solution systems at 25° C but at a 1.0 x 10-6 mole/liter manganese ion concentration. The Pourbaix Window diagrams depicted in Figures 1 and 2 were derived from the diagram presented in Atlas Of Electrochemical Equilibria in Aqueous Solutions," Marcel Pourbaix, pages 286-293, National Association of

10   Corrosion Engineers, Houston, Texas. The Eh and pH values as plotted on the graphs delineate the boundaries of the MnO_2 stability area for each of the two aqueous solution systems, emphasized with shading in Figures 1 and 2. A comparison of the boundaries of the two shaded areas on Figures 1 and 2 is illustrative of the different stability areas that exist under different system conditions.

15   In the methods and systems disclosed herein, the conditions or parameters of aqueous systems are maintained within the metal oxide stability area for the target metal oxide valence state with regard to electrochemical (oxidizing) potential (Eh) range and pH range at the prescribed system temperature at ambient atmospheric conditions in order to provide an Eh-pH combination to achieve stable solution equilibrium, as defined by the stability area as

20   delineated in, for example, a Pourbaix Window diagram, such as those depicted in Figures 1 and 2.

In a Pourbaix diagram, the metal oxide stability area is defined by the thermodynamically stable ranges or boundaries of pH-Eh combinations that promote the existence and formation of high valence metal oxides, for example MnO_2 (where manganese

25   has an average valence state close to +4), as the most thermodynamically stable form of metal oxide in an aqueous solution system. In the methods of the invention, the constituents of the aqueous solution systems are the loaded oxides of metal and their disassociated metal salts along with the oxidizer or oxidizers in the aqueous oxidizing solution and the base or acids that may be added thereto. During processing, aqueous solution system conditions must be

30   moved to and maintained at or within the boundary area delineated by the combination of Eh and pH ranges. In order to accomplish this, Eh and/or pH adjustments must be made through the addition of oxidizer, base or acid.

To this end, Applicants utilize a heated aqueous oxidizing solution to provide the oxidizer or oxidant. The oxidizer, for example, but not limited to, gaseous oxidizers may also be added directly to a sorbent slurry or solution contain disassociated reactions products, though this methodology is not preferred. The oxidizer must be able to provide the required electrochemical (oxidizing) potential (Eh) at the specified temperature and within the specified pH ranges to provide an Eh-pH combination to achieve stable aqueous solution system equilibrium within the metal oxide stability area for metal oxides of the target valence state. Suitable oxidizers to name a few include, but are not limited to, persulfates, such as potassium peroxidisulfate (K2S2O8), sodium peroxidisulfate (Na2S2O8), and ammonia peroxidisulfate ((NH4)2S2O8), chlorates, such as sodium chlorate (NaClO3), perchlorates such as sodium perchlorate (NaClO4), permanganates, such as potassium permanganate (KMnO4), oxygen (O2) or air, ozone (O3), peroxides, such as H2O2, and hypochlorites, such as sodium hypochlorite (NaOCl). Other oxidizers may be selected by those skilled in the art based upon their compatibility with the metal oxide and corresponding reaction products. Other oxidizers suitable for use in the methods of the invention will be apparent to those skilled in the art; it being understood that the electrochemical potential (Eh) of the heated aqueous oxidizing solution, and therefore the effectiveness of the methods of the invention, depends, in part, upon the strength of the oxidizer and/or the concentration of the oxidizer in the solution.

Depending upon the conditions and constituents of the aqueous solution system, the pH range of the boundary may be acidic, near neutral, or basic. In short, processing may be carried out over the full pH spectrum. However, the oxidizer strength or concentrations required at the extremes of the pH spectrum may make such processing uneconomic though nonetheless achievable. As the reactions proceed, metal oxide is being produced and the oxidizer is being consumed, the system may tend to shift away from the desired pH range, in which case the addition of a suitable base or acid will help accomplish the necessary adjustment to maintain the system within the appropriate Eh-pH range of the metal oxide stability area. Applicants have found it beneficial to maintain pH relatively constant during processing. Alternatively, the introduction of additional oxidizer to bring the system within the appropriate Eh range as pH drifts or shifts in the aqueous system may also beneficially accomplish the necessary adjustment. The aqueous solution system is, and therefore the methods and systems of the invention are, dynamic and adaptive with necessary adjustments

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being made not only by introduction of acid or base but with introduction of oxidizer as well.

Examples of useful bases include but are not limited to alkali or ammonium hydroxides, potassium hydroxides, and sodium hydroxides. Examples of useful bases include but are not limited to sulfuric, nitric, hydrochloric and perchloric acid to name a few. Applicants have found it useful to match the cations of the oxidant and base. For example, where the oxidant is a persulfate, such as potassium peroxodisulfate ($K_2S_2O_8$), the pH could be adjusted with a compatible or suitable base, such as potassium hydroxide (KOH). If sodium peroxodisulfate is used ($Na_2S_2O_8$), a compatible base would be sodium hydroxide (NaOH); and with ammonium peroxodisulfate (($NH_4)_2S_2O_8$), ammonium hydroxide ((NH_4OH) would be a compatible base. The acids or bases and other process additives are generally commercially available and those skilled in the art would be able to readily identify compatible process additives useful within the scope of the invention.

Using manganese as an example, Applicants are able to achieve stable and controlled precipitation so as to rapidly and adaptively yield oxides of manganese having equal or increased loading capacity when compared to the untreated commercially available EMD and CMD oxides of manganese (NMD, EMD, and CMD) or when compared to virgin oxides of manganese. At a given pH, Eh and temperature ranges within the MnO_2 stability area, the desired manganese valence state (theoretically close to +4) will exist. Thus, there is no propensity for Mn compounds at or close to +4 valence state to degrade to +3 or +2 valence states. However, if conditions are not maintained within the MnO_2 stability area such degradation may occur. Applicants have found that oxides of manganese precipitated from a heated oxidizing solution maintained within the MnO_2 stability area will exhibit a Mn valence state of close to +4 and exhibit target pollutant loading capacities equal to and/or greater than (increased) the loading capacities of virgin oxides of manganese.

As further discussed below heated oxidizing solutions having the desired pH-Eh-temperature combination can be prepared and maintained or adjusted by increasing or decreasing oxidizer, acid or base concentrations and/or temperature adjustment, as appropriate, so that the conditions are adjusted to remain within the metal oxide stability area. With monitoring of Eh, pH, and temperature, an operator can make necessary adjustments in order to maintain or return the oxidizing solution to conditions within the metal oxide stability area. Such monitoring and adjusting can also be automated utilizing electronic probes or sensors and controllers as discussed later herein below.

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In the various embodiments of the invention disclosed herein, the systems in which the methods of the invention are carried out all have common or corresponding components that are substantially the same. Though referred to, in appropriate instances by slightly different terms (for purposes of clarity) and being identified with corresponding but different

5   reference numbers in the figures and the disclosure herein below, their operation and function will also be understood to be substantially the same and equivalent. To the extent that there are operational or functional differences, they are identified and discussed as appropriate. The common system components include oxidation vessels in which regeneration, pretreatment and precipitation are carried out; agitation devices and probes for temperature,

10   Eh and ph measurement with which the oxidation vessels are equipped, filtration units, and rinses. Heaters supply heat to the process streams which enter the oxidation vessels and the oxidation vessels are also equipped with a heater (heaters not shown in the figure hereof) for adding heat to and maintaining the temperature of the solutions in the vessels. For applications requiring dried oxides of metal, a dryer would be another common component.

15   And, for applications requiring the oxides of metal to be comminuted and sized, a comminuting device would be another common component. These components are further discussed herein below. It should be understood that discussion of these components in the first instance with respect to one embodiment of the invention is equally applicable and relevant to the components as incorporated into the other embodiments of the invention.

20   Therefore, in the interest of efficiency and to avoid undue repetition, the discussion of the components may not be serially repeated in detail.

Turning to Figure 3, a precipitation system 50 is shown. The recovered metal values in Figure 3 are introduced or conveyed to precipitation vessel 54 which is equipped with an agitator 55, also referred to herein as an agitation means 55. Any of various agitation devices

25   known to those skilled in the art to be suitable for agitating, mixing and stirring the solid-liquid slurries so as to keep the solid oxides of metal particles generally suspended in the solution can be utilized. As illustrated in Figure 3, vessel 54 is optionally equipped with temperature, probe 53A, pH probe 53B and Eh probe 53C. These probes are utilized to measure their respective parameters in the heated aqueous oxidizing solution and may be in

30   electronic communication with a controller as later discussed herein with reference to Figure 4.

In the vessel 54, the recovered metal values are mixed with a heated oxidizing aqueous solution. The heated aqueous oxidizing solution and the recovered metal value

solution are preferably preheated to temperatures at or near the boiling point of aqueous solutions at atmospheric pressure or other operational pressure. The heating of the two constituent solutions prior to mixture serves to avoid or minimize the precipitation of undesired oxides of metal and also serves to provide for fairly rapid processing times. The heated oxidizing solution is so prepared as to have conditions that move the mixture between it, the acid or base solution, and the recovered metal value solution toward the metal oxide stability area. For example, at sea level, this would be about 100 °C. Oxidation and precipitation may be carried out at temperatures ranging from about 90 °C to about 110 °C, with temperatures between 95 °C to about 108°C being preferred, and temperatures between about 100°C to about 105°C being more preferred at sea level atmospheric pressures. The solution temperature should be maintained unless a temperature adjustment away from near boiling is required in order to maintain the aqueous solution system within the metal oxide stability area as other system parameters shift during processing. Determining which parameter adjustments to make is a matter of engineering or operator choice as long as the adjustment moves system conditions into or maintains those conditions within the metal oxide stability area.

For the recovered metal values, the heated aqueous oxidizing solution provides the required electrochemical (oxidizing) potential (Eh), within the specified temperature and pH range to yield metal oxides having pollutant loading capacities and/or oxidations states equal to or greater than that of the metal oxides in the ore or other raw material. Under agitation, the slurry formed in the precipitation vessel 34 as the metal oxides precipitate is continuously mixed and the pH of the slurry is adjusted by appropriate means, e.g., addition of acid or base. The metal oxides are allowed to remain within the slurry for a time sufficient to achieve an increased oxidation state and/or a target pollution loading capacity equal or greater than that of virgin metal oxides. At or near the sea level atmospheric pressures, a sufficient time may be between about 20 minutes to about 70 minutes, preferably between about 35 minutes to about 55 minutes, and more preferably between about 40 minutes to about 50 minutes. Such processing times are rapid compared to the hours and tens of hours of sometimes staged processing of prior art methods. Applicants have found that an optimal time for the precipitated metal oxides to remain in the precipitation vessel (34) is approximately 45 minutes, during which time the precipitated metal oxides have their average valence state increased. Manganese oxides, for example, are oxidized up to valance states close to +4. A deviation of two to three minutes above or below 45 minutes is near

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enough to optimal to provide metal oxides having oxidation states and/or loading capacities particularly suitable for use as a sorbent for target pollutant removal. It being understood that with greater deviations from the optimal time but yet within the above stated time ranges oxides of manganese suitable pollutant removal (particularly when high loading capacity is

5   not required) and for other uses may nonetheless be produced with the invention

Separation of the precipitated oxides of metal and the oxidation filtrate is best preformed at close to operating temperature in precipitation vessel 34, or close to about 100 °C. Allowing the solution containing reformed oxides of manganese and the aqueous oxidizing solution to cool to temperatures below the solubility temperatures for residual ions

10   in solution, for example, but not limited to $K+1$ and $SO4-2$ can result in the precipitation of solid salts such as $K2SO4$. Through experimentation, it has been recorded that allowing salts to precipitate with the precipitated oxides of metal sorbent lowers the target removal efficiency and loading rates and should therefore be avoided.

The precipitated metal oxide sorbent is then rinsed with water to wash away any

15   remaining spectator ions. In Figure 3 this is illustrated as two separate steps: 1) filtering and separating the precipitated oxides of metal from the aqueous oxidizing solution to provide an oxidation filtrate in filtration unit 56; and 2) rinsing the sorbent with water to wash away remaining spectator ions in the sorbent precipitation rinse 57. Any of a variety of suitable filtration techniques and devices known to those skilled in the art may be utilized for this

20   purpose. It should be noted that the filtration and rinsing step could be combined using filtration and rinsing equipment known to those skilled in the art. Further, the filtration unit 56 may alternatively be incorporated into and as part of the precipitation vessel 54.

The rinsing of the precipitated oxides of metal should be of sufficient duration and with sufficient volume of water as to remove dissolved ions associated with the oxidizer,

25   metal salt, base, and acid in the aqueous oxidizing solution to a suitable level. The presence of these ions in the precipitated sorbent in sufficient amounts may negatively impact the loading capacity or removal efficiency of the precipitated oxides of metal. This is not to say that precipitated oxides of metal that are not so rinsed will be ineffective for removal of target pollutants because in fact they may be so utilized without the rinse and good removal rates

30   can be achieved. However, the precipitated oxides of metal may be more efficiently utilized following rinsing.

Various measurement techniques and devices known to those skilled in the art can be employed to determine the level or concentration of such ions in rinse water and thereby

determine whether the oxides of metal have been adequately rinsed.   Such techniques include measurement of conductivity, resistivity, total dissolve solids (TDS) or other indicators of the level of disassociated ions and/or dissolved solids and fine particulates in a solution, such as specific gravity or density or chemical analysis. By way of example and not

5   limitation, TDS measurements of the oxidation filtrate taken by Applicants have been in the range of 80,000-200,000, representing the disassociated ions from the oxidant, metal salt, base or acid and other possible dissolved solids or fine particulates associated with the precipitation. The rinse step should generally being designed to remove such ions, solids and particulates from the precipitated oxides of metal to an acceptable level or tolerance. Where

10   precision is required the vessel or apparatus in which the rinse is carried out should be equipped with an appropriate measurement device for conductivity, resistivity, TDS level or other indicator. With monitoring of such measurements, the rinse step can be carried out until the oxidation filtrate reaches the desired level based upon the measurement technique employed. Through a series of precipitation cycles and use cycles, the acceptable level or

15   tolerance for the given use to which the precipitated oxide will be put can be determined, as well as the volume, flow rate and duration of the rinse in order to establish or standardize operating procedures. Although lowering the TDS of the filtrate generally favorably impacts target pollutant removal efficiency and loading rates, Applicants have found that oxides of metal prepared according to the methods of the invention may be utilized for target pollutant

20   removal with or without the rinsing step. Applicants have achieved adequate target pollutant removal with precipitated oxides of metal that is not rinsed prior to use as a sorbent, but have seen better removal at measured TDS levels in the filtrate of less than 100,000 and even better performance at less than 10,000.

Returning to Figure 3, the wet precipitated oxides of metal, if being utilized in a dry

25   target pollutant removal system such as the Pahlman™ system, is first routed for drying to a dryer 58. Oxides of metal may be introduced into pollution removal systems as a dry power, a wet filter cake, or a slurry by a slurry or spray feeder. In dry removal systems, the wet filter cake and sprayed slurry may be "flash dried" upon contact with industrial gas streams which may be introduced at elevated temperatures into the pollutant removal systems. For such

30   applications the drying step may not be necessary and the wet or moist filter cake may be conveyed to a filter cake feeder. Similarly, with slurry or spray feeders, once adequately rinsed, the precipitated oxides of metal need not be filtered or separated. Rather, they can be conveyed as a slurry to the feeder. However, when the oxide of metal sorbent is to be

introduced as a dry particulate or powder, both drying and comminuting to size of the oxides of metal particles is typically performed. The dryer 58 may be a kiln or other suitable dryer used for such purposes and known to those skilled in the art. The dryer 58 may utilize waste heat generated by combustion which is transferred or exchanged from combustion or process

5   gases at an industrial or utility plant. When drying is required the temperature should be below the thermal decomposition temperature of the oxides of metal but sufficiently high so as to drive off surface water or moisture without removing any waters of hydration or water of crystallization. As an illustrative example only, temperatures around 100 °C to 160 °C have been found to be adequate for this purpose for manganese oxide. Drying can be

10   conducted at lower temperatures but drying time may be uneconomically extended; and at higher temperatures, which can be utilized in Applicants' invention, short drying time will have to be closely observed so as to avoid thermal decomposition of the oxides of metal, driving off structural water, or undesired damage to the crystalline structure of the oxides of metal.

15   Precipitated oxides of metal may be filtered, decanted or otherwise collected and dried. If further oxidation of the precipitated oxides of metal is required, the drying step may be carried out in an oxidizing atmosphere. Alternatively, in accordance with the methods of the invention, an oxidizer, as previously described may be introduced into vessel 50 while the oxides of metal are being formed and precipitated. For example air or oxygen can be bubbled

20   through or a persulfate or other suitable oxidizer may be used. In the production of a manganese sorbent, for example, the newly precipitated oxides of manganese have a valence state close to 4+ and an oxidation strength in the range of 1.5 to 2.0, preferably 1.7 to 2.0, and has a BET value ranging from about 1 to 1000m2/gr. With comminuting, oxides of manganese particles can be sized for industrial and chemical application uses and particularly

25   a particle size ranging from 0.5 to about 500 microns and be sent to the sorbent feeder for reuse in removal of target pollutants.

           Use of acoustic energy during processing particularly during precipitation may favorably affect the performance of the oxides of metal produced in the various embodiment of the invention. Acoustic energy, as applied industrially, includes the range from ultrasonic,

30   which is short-wave, high-frequency (greater than 20,000 Hz.) energy, to infrasonic, which is long-wave, low-frequency (less than 20 Hz.) energy. All forms of acoustic energy are transmitted as pressure waves, and are usually generated by specialized devices or

transducers which convert electricity or pressurized air into acoustic energy within the desired frequency range.

Industrial applications of ultrasonic acoustic energy include agitation of liquid solutions for applications such as solvent parts cleaning for example. Infrasonic acoustic energy, for example, is used to loosen material in dry powder transport systems, to promote smooth flow and prevent stoppage of the material, or to remove filter cake from bag-type filters; it is not typically used in liquid applications. These and other applications of such technology may also be methods of transferring energy to a solution, gas, or solid material, without raising its temperature.

There are many commercial manufacturers of ultrasonic equipment such as small or laboratory scale ultrasonic equipment like those available from the Cole-Parmer Instrument Company and large scale equipment, such as high pressure and /or high temperature device available from Misonix.

With the application of acoustic energy in the form of ultrasonic or infrasonic waves has improvements in sorbent activity or loading capacity can be achieved. The application of acoustic energy during processing of oxides of metal may be doing all or some of the following actions: (1) enhancing agitation during sorbent processing to improve reaction rates and enhance mixing; (2) increasing dissolution rates of chemicals used in the processing of oxides of metal; (3) altering structural development of crystal structure during and following precipitation from solution; and (4) breaking up large oxides of metal crystal formations. In the methods and systems of the invention, acoustic energy would be generated by specialized devices or transducers and directed which may optionally be incorporated into the precipitation vessel 54. Such sonication devices may be used and incorporated into other system components, such as oxidant, acid or base vessels or vessel in which metal salts are mixed with water prior to precipitation processing.

Monitoring and adjustment of the conditions of the precipitation vessels employed in the different embodiments of the invention are carried out utilizing electronic controls. Figures 4-6 illustrate embodiments of the invention incorporating an electronic controller 67 to provide adaptive integrated simultaneous monitoring and adjustment of operational parameters, e.g., temperature, Eh, and pH, within the oxidations vessels with an optional feed back loop for checking the loading capacity of the oxides of metal produced according the methods of the invention. In Figures 4-6, embodiments of the precipitation system are

depicted as being integrated with a pollutant removal system 60 that utilizes oxides of metal as a sorbent for target pollutant removal.

The system 60 is presented a representation of pollutant removal systems in general and it should be understood that the system 60 could be a wet scrubbing removal system, a dry removal system or a combination thereof. System 60 as represented includes a reaction chamber 62 and a sorbent feeder 64 which contains and/or is configured to feed oxides of metal to the reaction chamber 62. Depending upon the type of reaction chamber, oxides of metal may be fed as a dry powder or dry particles, as a slurry, or as a wet filter cake. Viewed as a representation of a Pahlman™ removal system, a stream of untreated gas containing target pollutants is shown entering into the reaction chamber 62. In this system 60, gas and sorbent oxides of metal are introduced into the reaction chamber 62 and contacted under conditions and for a time sufficient to effect removal of the target pollutant(s) at a targeted removal efficiency rate for the target pollutant(s). It should be understood that the gas and the oxides of metal may be introduced together or separately into reaction chamber 62, depending upon the type pollutant removal system and type of reaction chamber employed. Clean gas, gas from which a target pollutant has been removed, is shown to be vented from the reaction chamber 62. Loaded oxides of metal will be removed from the reaction chamber, as dry reacted sorbent, a filter cake of reacted sorbent or a slurry of reacted sorbent and conveyed for regeneration and/or precipitation processing with appropriate handling.

Described in greater detail, the Pahlman™ system may be viewed as being comprised of a feeder containing a supply of sorbent or oxides of metal, at least one bag house configured to receive sorbent and a gas containing target pollutants, such as those identified herein above. Gas is introduced at temperatures ranging from ambient temperature to below the thermal decomposition or liquification temperature of metal salt reaction products formed between the oxides of metal and the target pollutant. Gases are introduced into the bag house and contacted with the sorbent for a time sufficient to effect capture of the target pollutant at a targeted pollutant capture rate. The target pollutant or pollutants are captured through formation of the reaction product between the target pollutant and the sorbent. The system will also include a controller for simultaneously monitoring and adjusting system operational parameters. The controller provides integrated control of system differential pressure and other operational parameters selected from the including, but not limited to, target pollutant capture rates, gas inlet temperatures, sorbent feeder rates and any combinations thereof. Differential pressure within the system is regulated by the controller so that any differential

pressure across the system is no greater than a predetermined level and the target pollutant is removed at the targeted pollutant capture rate set point.

The system may incorporate more than one reaction zone, both of which may be bag houses. Alternatively, the system may optionally incorporate a reaction zone upstream of a bag house into which gas and sorbent are introduced and subsequently directed to the bag house. Such optional reaction zones may be selected from the group of reaction zones that includes a fluidized bed, a pseudo-fluidized bed, a reaction column, a fixed bed, a moving bed, a serpentine reactor, a section of pipe or duct and a cyclone or multi-clone. When two reaction zones are thus connected and the gas stream contains at least two target pollutants, such as SO_x and NO_x, for example, the first target pollutant may be captured or removed in the first reaction zone or substantially removed in the first reaction zone and the second target pollutant will be removed in the second reaction zone. This can be advantageously utilized, particularly where the two reaction zones are bag houses to capture a first target pollutant such as SO_x in the first reaction zone and a second target pollutant such as NO_x in the second reaction zone. This would allow for separate regeneration of loaded sorbent having reaction products thereon from reaction between oxides of metal and a single target pollutant or at least different target pollutants that are captured in the second bag house. Thus, if the target pollutants are SO_x and NO_x this would allow for separate regeneration and filtration of a SO_x loaded sorbent and NO_x sorbent with their respective reaction product ions being disassociated into separate pre-oxidation rinses with the resultant pre-oxidation filtrates also being separately processed to precipitate out oxides of metal. The respective precipitation filtrates would then allow for separate production of sulfate by-products and nitrate by-products.

With reference to Figure 4, a precipitation system 30 substantially as depicted in Figure 3 is illustrated in block flow and is connected to removal system 60. Precipitation vessel 34 is equipped with temperature probe 33A, pH probe 33B, and Eh probe 33C; regeneration vessel 14 is equipped with temperature probe 13A, pH probe 13B, and Eh probe 13C all of which are in electronic communication with a controller 67. An acid and/or base vessel (not shown) is configured to feed acid and or base to precipitation vessel 34 and regeneration vessel 14. An oxidant vessel containing oxidizing solution (not shown) is configured to feed oxidizing solution to precipitation vessel 34 and regeneration vessel 14. Loaded sorbent may conveyed directly from reaction chamber 62 to regeneration pre-oxidation rinse 12 or it may be directed to a loaded sorbent vessel (not shown) for holding

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and subsequently conveyed to rinse device 12. The pre-oxidation filtrate from rinse 12 is routed to precipitation vessel 34. The recovered metal values from the metal ore are added to precipitation vessel 34 to provide make up metal oxide to the system. The rinsed sorbent from pre-oxidation rinse device 12 is routed to the regeneration vessel 14. The feeders (not

5   shown) of acid and/or base vessel, oxidant vessel, and loaded sorbent vessels (not shown) are in electronic communication with the controller 67. The controller 67 is also in electronic communication with the Eh probe 33C, pH probe 33B, and temperature probe 33A with which the precipitation vessel 30 is equipped and Eh probe 13C, pH probe 13B, and temperature probe 13A with which the regeneration vessel 14 is equipped. As illustrated,

10   newly precipitated or virgin sorbent from the precipitation vessel 34 and regenerated sorbent from the regeneration vessel 14 is routed to filtration unit 16 for filtering. The sorbent is further routed to the rinse device 17 to be further rinsed. Alternatively, filtration unit 16 and rinse 17 may be combined into one device so as to remove filtrate and rinse in a combined operation. Also, sorbent from the precipitation vessel 34 and the sorbent from regeneration

15   vessel 14 may each have its own filtration device and processed sorbent rinse device. Sorbent is then routed to the sorbent dryer 18 As illustrated, sorbent from sorbent dryer 18 is routed to comminuting device 19 and then to sorbent feeder 64 which in turn feeds the sorbent to reaction chamber 62. Alternatively, sorbent from dryer 18 may be routed directly to reaction chamber 62 or to a sorbent storage vessel prior to being directed to the feeder 64.

20   Reaction chamber 62 is equipped with optional target pollutant concentration readers or continuous emission monitors (CEMS) for NOX and SO2, readers 68A and 68B, which are in electronic communication with controller 67. It should be understood the reaction chamber 62 may be equipped with other equivalent readers where different target pollutants are being captured.

25   The controller 67 interfaces with precipitation vessel 34 probes 33A, 33B, and 33C; NOx and SO2 readers 68A and 68B and oxidant, base and or acid feeders and vessels (not shown) for measurement and adjustment of operational parameters with in the vessels 14 and 34. The controller 67 signals the addition of oxidant, acid, and or base to precipitation vessel 34 based upon the inputs received from the probes until the desired Eh/pH reading is obtained

30   prior to addition of the pre-oxidation filtrate into the precipitation vessel 34. Agitator 35 continuously agitates the solution. The temperature, pH, and Eh of the precipitation vessel 34 are monitored and adjusted continuously so as to maintain conditions within the metal oxide stability area.

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The controller 67 similarly interfaces with regeneration vessel 14 probes 13A, 13B, and 13C; NOX and SO2 readers 68A and 68B and oxidant, base and or acid feeders and vessels (not shown) for measurement and adjustment of operational parameters within the vessel 14. Thus, temperature, pH, and Eh of the aqueous oxidizing solution in regeneration vessel 14 are monitored and adjusted continuously so as to maintain conditions within the metal oxide stability area.

Precipitation vessel 34 and regeneration vessel 14 may be run in parallel operation or alternating operation so as to be able to verify sorbent loading capability using the optional feedback loop of the controller 67and probes 68A and 68B.

The controller 67 contains a programmable logic controller (PLC) and other hardware components necessary for the operation of the controller such as a power supply, input and output modules that would communicate with the probes 33A, 33B, and 33C; probes 13A, 13B, and 13C and/or readers 68A and 68B, and with the oxidant, base and/or acid feeder and vessels (not shown), and loaded sorbent feeder (not shown). The controller 67 receives inputs from the various probes and readers and converts them into ladder logic language that would be used by an internal proportional integral derivative (PID) loop to individually and simultaneously monitor system operational parameters and to reconcile the inputs with predetermined or computer generated calculated set points for the operational parameters, such as temperature, and Eh and pH levels. As determined by computer logic, the controller 67 will send an output as necessary to any of the feeders of oxidant and base and/or acid vessels (not shown) signaling a feeder to cycle on or to change feeder rate so as to maintain or adjust system operational parameters to within the metal oxide stability area for either precipitation vessel 34 or regeneration vessel 14. The controller 67 may also contain an Ethernet card or other component that allows onsite or offsite remote display and operator interface and control as needed.

The controller 67 would be given a start command and direct the loaded sorbent feeder (not shown) to inject predetermined amounts of loaded sorbent into the pre-oxidation rinse device 12. The controller 67 signal injection of a predetermined amount of oxidizing solution, acid and/or base into the precipitation vessel 34 and regeneration vessel 14 checking and or adjusting the Eh and/or pH of the solution prior to feeding in the predetermined amount of pre-oxidation filtrate from the pre-oxidation rinse device 12 into the precipitation vessel 34 and a predetermined amount of rinsed sorbent from the pre-oxidation rinse device 12 into the regeneration vessel 14. The Eh of the oxidizing solution in precipitation vessel 34

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and regeneration vessel 14 may be adjusted by addition of an oxidizer in sufficient quantity as to raise the Eh to the desired level from an oxidizer vessel (not shown), containing a supply of oxidizer or aqueous oxidizing solution. As determined by programmed controller logic, the controller 67 would also check, based on inputs received from the precipitation

5   vessel 34 probes 33A, 33B, and 33C; and regeneration vessel 14 probes 13A,13B, and 13C and/or adjust the conditions of the precipitation vessel 34 and regeneration vessel 14 by adjusting the temperature utilizing a heater or heat exchanger (not shown) to increase or decrease solution temperature; the pH, if needed, by increasing or decreasing the rate of base or acid feed; and the Eh, if needed, by increasing or decreasing the oxidizer concentration of

10 the aqueous oxidizing solution. An optional, final quality control loop is provided utilizing the readers 68A and 68B checking the loading performance of the processed oxides of metal sorbent by sending, for example, SOx and NOx readings back to the controller 67. As determined by controller logic, the controller 67 would then adjust the precipitation vessel 34 and regeneration vessel 14 parameters, if needed, to provide precipitated oxides of metal and

15 regenerated oxides of metal, respectively, capable of removing target pollutants at the targeted removal rates. The same controller may also be used to control the entire operation of the removal system 60, the regeneration system 10 and the precipitation system 34 and their components as discussed above including, pre-oxidation rinse 12, filtration unit 16, rinse device 17, dryer 18, comminuting device 19, sorbent feeder device 64 and the by-products

20 processing vessel 66, or separate controllers may be provided.

With reference to Figure 5, the regeneration and precipitation system 20 is depicted as integrated with removal system 60. The controller 67 will be in electronic communication with the probes of a single oxidation vessel, vessel 24; otherwise, the operation and function of the electronic control and communication is substantially the same as described above with

25 respect to Figure 4. With reference to Figure 6, this is equally applicable to the integration of systems 30 and 60 to the electronic communication and control of the corresponding system components. Note that a variation of regeneration and precipitation method is illustrated. In Figure 6, reacted sorbent is rinsed and filtered and routed to dryer 18. It is not direct to a regeneration vessel but the pre-oxidation filtrate is routed to precipitation vessel 34 where

30 precipitation is carried out as previously described. This variation of the method of the invention can be used where the loading capacity oxides of metal below the reaction product surface coating on the sorbent particles has not been significantly diminished during pollutant removal as to require chemical regeneration. In such cases, it is sufficient to wash away the

reaction products, dissolving and disassociating them into the rinse solution or pre-oxidation filtrate and the rinse oxides of metal can then be dried and comminuted if necessary prior to be reused to capture target pollutants. Applicants have found SOX to be one such target pollutant; and that where the gas stream contains primarily concentrations of this pollutant a

5   rinsing is all that is required prior to reuse of the rinsed sorbent, with recover of reaction product ions through precipitation and other processing.

Two examples are provided to illustrate the precipitation of oxides of manganese utilizing the methods of the applicants' invention. The examples are provided for illustration purposes and not intended to narrow the scope of the applicants' invention. Both examples 1

10   and 2 use manganese sulfate (MnSO4*H2O) as the Mn+2 salt, potassium persulfate (K2S2O8) as the oxidizing agent, and potassium hydroxide (KOH) as the compatible pH adjusting base. The two examples serve to illustrate precipitation from leachate. Example 1 outlines procedures to produce lab quantities (100 grams) of virgin oxides of manganese sorbent with Example 2 outlining large industrial quantities (50 pounds) of virgin oxides of

15   manganese sorbent. Figure 3, can be referenced in both examples 1 and 2.

Example 1

Turning now to precipitation example 1, in the precipitation vessel, 169 grams (1 mole) of MnSO4*H2O and 750 milliliters of water were mixed and heated to 100oC. In the

20   oxidant vessel, 376 grams (1.4 moles) of K2S2O8 and 1000 milliliters of water were mixed and heated to 80oC. The oxidizing solution was rapidly added to the manganese salt solution in the precipitation vessel and vigorously stirred while the solution was quickly heated to boil and maintained at not less than 100oC. Immediately following addition of oxidant to the precipitation vessel, potassium hydroxide (20% KOH) was added with an adjustable-flow

25   fluid pump for the purpose of controlling the pH of the solution at a target pH level of 1.85, within 0.02 pH units. Solution pH and Eh readings during the course of the precipitation reaction are presented in Figure 9. The precipitation vessel was continually mixed and the temperature maintained at not less than 100oC for 45 minutes after the combined solutions of manganese sulfate and potassium persulfate reached a boil. Following the 45 minute reaction

30   time, the slurry solution was poured into a Beuchner funnel equipped with a No.5 Whatman filter paper for vacuum filtration to separate the newly precipitated oxides of manganese from the clear oxidation filtrate. The precipitated sorbent was then rinsed with clean water until filtrate total dissolved solids (TDS) was approximately 1000 ppm. The filter cake was then

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placed in an electric oven and dried at 127oC for 9 hours. The dried oxides of manganese was then de-agglomerated and passed through an 80 mesh sieving screen.

Upon analysis of the newly precipitated oxides of manganese from example 1, both physical and chemical characteristics were determined and target pollutant loading rate testing was preformed. The average particle size was found to be 91.2 microns, with a range of 0.3 to 250 microns. The bulk density was measured to be 0.202 grams/cc with a true specific gravity of 4.246 grams/cc. The precipitation resulted in oxides of manganese with an extremely large surface area. Surface area (BET) was measured to be 271m2/gram. Contributing to the large surface area, would be the average pore volume, measured to be 0.984cm2/gram and the average pore diameter, which was found to be 0.0145 microns. Chemical composition analysis was also conducted and the % by weight constituents were measured as follows: 52.1 % manganese (Mn), 3.82 % potassium (K), 16.4 % structural water (H2O), 4.3 % adsorbed water (H2O), and the balance, determined by difference, to be 23.38 % oxygen (O).

Oxides of manganese having the formula MnOX where X is about 1.5 to about 2.0 are particularly suitable for dry removal of target pollutants from gas streams. However, the most active types of oxides of manganese for use as a sorbent for target pollutant removal usually have the formula MnO1.7 to 1.95, which translates into manganese valence states of +3.4 to +3.9, as opposed to the theoretical +4.0 state. Upon analysis, it was found that the newly precipitated oxides of manganese sorbent created in example 1 exhibits a valance state of 3.52, which translates into: MnO1.76.

Example 2

In example 2, a 50 pound quantity of newly precipitated oxides of manganese sorbent was prepared. Precipitation of the 50 pound batch was conducted following the same techniques and procedures as the 100 gram precipitation outlined in example 1 and the pH and Eh values during the precipitation are illustrated in figure 9, with the exception being the target pH level set point and the strength of the KOH solution. In the precipitation vessel, 84.5 lbs of MnSO4*H2O and 45 gallons of water were mixed and heated to 100oC. In the oxidant vessel, 188 lbs of K2S2O8 and 60 gallons of water were mixed and heated to 80oC. Immediately following addition of oxidant to the precipitation vessel, potassium hydroxide (for example 2, 46% KOH) was added with an adjustable-flow fluid pump for the purpose of controlling the pH of the solution at a target pH level of 3.5, within 0.02 pH units. The

remaining oxides of manganese precipitation steps were conducted exactly as with example 1, just on a larger scale. For example 2, a one cubic foot capacity membrane filter press was utilized to both filter the precipitate from the oxidation filtrate and to rinse the newly precipitated oxides of manganese with clean water to obtain the desired level of filtrate TDS.

5   Upon analysis of the newly precipitated oxides of manganese from example 2, both physical and chemical characteristics were determined and target pollutant loading rate testing was preformed. The average particle size was found to be 92.5 microns, with a range of 0.2 to 300 microns. The bulk density was measured to be 0.404 grams/cc with a true specific gravity of 3.5 grams/cc. The precipitated oxides of manganese of example 2 was

10   produced using a higher pH set point of 3.5, resulting in precipitated oxides of manganese with a higher surface area than was produced with a pH set point of 1.85, as in example 1. Surface area (BET) was measured to be 312m2/gram. Average pore volume was measured to be 0.640cm2/gram and the average pore diameter was found to be 0.0082 microns. Chemical composition analysis was also conducted and the % by weight constituents were measured as

15   follows: 48.9 % manganese (Mn), 6.81 % potassium (K), 18.0 % structural water (H2O), 1.0 % adsorbed water (H2O), and the balance, determined by difference, to be 25.29 % oxygen (O). Additionally, upon analysis, it was found that the newly precipitated oxides of manganese sorbent created in example 2 exhibited a valance state of 3.54, which translates into: MnO1.77.

20   Without being limited by belief or theory, Applicants believe, based upon the chemical composition data for precipitation Examples 1 and 2, that the oxides of manganese compound formed may be a mixture of cryptomelane (KMnO8O16), potassic manganese dioxide monohydrate (K)MnO2*H2O, and/or potassic vernadite ((K)MnO2*yH20). Regardless of the actual chemical designation, applicants have found the resulting oxides of

25   manganese species to be useful to exhibit high loading capacities for target pollutant capture or removal.

Applicants conducted a series of lab-scale tests utilizing a live slipstream of an actual exhaust gas from a coal-fired combustion source in order to demonstrate the increased loaded capacity achieved with the invention as compared to loading capacity of commercially

30   available oxides of manganese. Manganese dioxides are divided into three origin-based categories, which are: 1) natural (mineral) manganese dioxide (NMD), 2) chemical manganese dioxide (CMD), and 3) electrolytic manganese dioxide (EMD). As implied, NMD occurs naturally as various minerals, which may be purified by mechanical or chemical

means. The most common form of NMD is pyrolusite (β-MnO2), which is inexpensive, but has rather low chemical activity and therefore low pollutant loading capacity. CMD and EMD varieties are synthetic oxides of manganese. EMD is produced primarily for the battery industry, which requires relatively high bulk density (which often results from relatively

5   large, compact particles), relatively high purity, and good electrochemical activity. Though useful as sorbent, characteristics such as low surface area and large compact particle size make EMD somewhat inferior to CMD for gas removal applications, despite its good electrochemical activity. Chemically synthesized oxides of manganese of all kinds fall into the CMD category and includes chemically treated or pretreated oxides of manganese. In

10   chemical synthesis, a great deal of control is possible over physical characteristics such as particle size and shape, porosity, composition, surface area, and bulk density in addition to electrochemical or oxidation potential. It is believed that these characteristics contribute to the loading capacity of some oxides of manganese.

A glass reactor designed to mimic the gas-solid interactions known to be present in

15   the reaction zones of a Pahlman™ dry target pollutant removal system was utilized for the tests. The glass reactor was a vertically positioned Pyrex™ glass cylinder having an internal diameter of 2 inches and a length of approximately 18 inches. For each test run, 25.0 grams of oxides of manganese were suspended in the reactor using a permeable fritted glass filter, positioned approximately 4 inches from the bottom of the reactor, allowing for flow of the

20   gas stream through the reactor while keeping the oxides of manganese suspended. The test reactor was insulated and configured with thermocouples for temperature readings and heating elements for temperature control to maintain a temperature set point, which in the purposes of the conducted testes was 280°F.

A NOx and SO2 laden gas stream was pumped into the bottom of the test reactor at a

25   flow rate which provided adequate fluidization of the bed of sorbent to promote optimal gas/solids contact. The reactor was heated during the testing to 280°F and the gas flow rate was metered at a constant 6.5 liters per minute (lpm). The slipstream of actual exhaust gas was from a 570 MW tangentially-fired coal-burning boiler operating on Powder River Basin (PRB) western coal.

30   The composition of the exhaust gas was measured both on the inlet and outlet of the test reactor with appropriate gas analyzers, as one skilled in the art would employ and for the test run examples presented found to be within the following ranges: Oxygen (O2) 5.8-6.5%, carbon dioxide (CO2) 10-12%, oxides of nitrogen (NOx) 237-300ppm, sulfur dioxide (SO2)

207-455ppm. The composition of the inlet gas to the test reactor varied slightly from test to test, therefore the data was normalized and presented as pounds (lbs) of NOx or SO2 into and out of the test reactor. The extent of NOx and SO2 loading was then calculated to determine the increased sorbent loading capacity of the precipitated sorbent as compared to

5   commercially available oxides of manganese. The slipstream of the NOx and SO2 laden gas stream was passed through the fluidized bed of oxides of manganese, where the flow carried a portion of the sorbent up onto a sintered metal filter, thus creating a filter cake, which mimics a bag house reaction chamber of a Pahlman™ dry target pollutant removal system.

SO2 and NOX concentrations were measured continuously alternating from the

10 reactor inlet and outlet utilizing a continuous emissions monitoring system (CEMS). SO2 concentrations were measured utilizing a Bovar Western Research model 921NMP spectrophotometric instrument and NOX concentrations were measured utilizing a Thermo Electron model 42H chemiluminescent instrument. In order to obtain accurate and reliable emission concentrations, sampling and reporting was conducted in accordance with US EPA

15 Reference CFR 40, Part 60, Appendix A, Method 6C. Inlet gas temperature was 280° F, with a differential pressure across the permeable fritted glass filter of 2" of water. Figures 8 and 7 show the results of comparative loading rate test runs of four different virgin oxides of manganese samples conducted utilizing 25g each of: two commercially available forms EMD, CGM, and two forms precipitated utilizing methods of the applicants' invention.

20 Figure 8 shows the NOx loading curves. Looking now at Figure 8, EMD type oxides of manganese was at least achieving 90% NOx removal on a ppm basis for 12 minutes, during which time an accumulative total of 0.0451 grams of NOx entered into the laboratory test reactor with only 0.0029 grams of NOx exiting the reactor, for a total of 0.0422 grams of NOx being captured by the virgin EMD type oxides of manganese sorbent. CMD type oxides

25 of manganese was at least achieving 90% NOx removal on a ppm basis for 27 minutes, during which time an accumulative total of 0.1157 grams of NOx entered into the laboratory test reactor with only 0.0034 grams of NOx exiting the reactor, for a total of 0.1123 grams of NOx being captured by the virgin CMD type oxides of manganese sorbent. Precipitated sorbent example 1, which was previously described in this application, achieved 90% NOx

30 removal on a ppm basis for 102 minutes, with an accumulative total of 0.4372 grams of NOx entering the laboratory test reactor with only 0.0067 grams exiting, for a total of 0.4305 grams of NOx being captured by the oxides of manganese sorbent precipitated according to methods of the applicants invention. The second example provided (example 2) achieved

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90% NOx removal on a ppm basis for 181 minutes, with an accumulative total of 0.6801 grams of NOx entering the laboratory test reactor with only 0.0125 grams exiting, for a total of 0.6676 grams of NOx being captured by the oxides of manganese precipitated in example 2, detailed previously in this application. From the provided graph in figure 8 and the NOx

5   loading rates provided, applicants have illustrated the ability of the oxides of manganese precipitated according to this invention to exhibit substantially improved NOx loading rates, as compared to commercially available oxides of manganese

Figure 7 shows the SO2 loading curves. Looking now at Figure 7, EMD type oxides of manganese was at least achieving 99% SO2 removal on a ppm basis for 18 minutes, during

10   which time an accumulative total of 0.0999 grams of SO2 entered into the laboratory test reactor with only 0.0009 grams of SO2 exiting the reactor, for a total of 0.0990 grams of SO2 being captured by the virgin EMD type oxides of manganese sorbent. CMD type oxides of manganese was at least achieving 99% SO2 removal on a ppm basis for 36 minutes, during which time an accumulative total of 0.2022 grams of SO2 entered into the laboratory test

15   reactor with only 0.0011 grams of SO2 exiting the reactor, for a total of 0.2011 grams of SO2 being captured by the virgin CMD type oxides of manganese sorbent. Precipitated sorbent example 1, which was previously described in this application, achieved 99% SO2 removal on a ppm basis for 120 minutes, with an accumulative total of 0.5082 grams of SO2 entering the laboratory test reactor with only 0.0016 grams exiting, for a total of 0.5066 grams of SO2

20   being captured by the oxides of manganese sorbent precipitated according to methods of the applicants invention. The second example provided (example 2) achieved 99% SO2 removal on a ppm basis for 214 minutes, with an accumulative total of 1.6984 grams of SO2 entering the laboratory test reactor with only 0.0096 grams exiting, for a total of 1.688 grams of SO2 being captured by the oxides of manganese precipitated in example 2, detailed previously in

25   this application. From the provided graph in figure 7 and the SO2 loading rates provided, applicants have illustrated the ability of the oxides of manganese precipitated according to this invention to exhibit substantially improved loading rates for SO2, as compared to commercially available oxides of manganese

The data from the lab-scale tests presented in Figure 8 and 7 illustrate the increased

30   loading capacity for target pollutants NOx and SO2 that is achievable with the methods of the applicants' invention. Additionally, Figures 8 and 7 serve to illustrate the differential loading rates of target pollutants, specifically NOx and SO2. Looking at the loading rates of oxides of manganese precipitated in example 1, the loading rate for SO2 is approximately 2.5 times

the loading rate of NOx by weight; with SO2 in example 1 precipitated sorbent capturing 1.688 grams of SO2 at a 99% removal rate and 0.6676 grams of NOx at a 90% removal rate. The differential loading rates for NOx and SO2 are believed to be indicative of the reaction kinetics of the removal process when, in this example, oxides of manganese are used as a

5   sorbent.

       Figure 9 contains the ph and Eh values through time for precipitation of oxides of manganese reactions, as outlined above in examples 1 and 2. In both cases the pH was held constant at the pH set point for the duration of the approximate 45 minute production time. As is illustrated in example 1, where the pH set point of 1.85 was reached within two minutes

10   of the solution reaching 100°C, the Eh increased from 1150 to about 1380 within about 12 minutes. The Eh remained at about 1380 for the remainder of the 45 minute reaction time. By contrast example 2, where the pH set point of 3.5 was reached within two minutes of the solution reaching 100°C, the Eh increased to a lower value of 1325 within about 10 minutes. Both examples 1 and 2 were conducted with the same ratio of oxidant to manganese sulfate

15   and the pH set point resulted in differing Eh solution values. The data presented in Figure 9 serves to further illustrate the applicants' concept of adjusting the solution composition to produce oxides of manganese within the MnO2 stability window that exhibit increased target pollutant loading rates and how the MnO2 stability window will change as one moves through the possible pH range

20   As indicated above, Applicants have found it beneficial to maintain pH constant throughout processing according to the methods of the invention. Figure 9 plots ph and Eh values through time for precipitation of oxides of manganese reactions for Examples 1 and 2 above. In both cases after the aqueous oxidizing solution reached operating temperatures and an equilibrium point within the MnO2 stability area, the pH was held constant at the pH set

25   point for the duration of the approximate 45 minute production time. With respect to Example 1, where the pH set point of 1.85 was reached within two minutes of the solution reaching 100°C, the Eh increased from 1150 to about 1380 within about 12 minutes. The Eh remained at about 1380 for the remainder of the 45 minute reaction time. By contrast in Example 2, where the pH set point of 3.5 was reached within two minutes of the solution

30   reaching 100°C, the Eh increased to a lower value of 1325 within about 10 minutes. Both Examples 1 and 2 were conducted with the same ratio of oxidant to manganese sulfate; however, their respective pH set points resulted in differing Eh solution values. The data presented in Figure 9 , serves to further illustrate the Applicants' concept of adjusting and

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maintaining the solution conditions to produce oxides of manganese within the MnO2 stability area that exhibit increased target pollutant loading rates and/or valences stats and how the MnO2 stability area will change as one moves through the possible pH range

Applicants have found that by not holding the pH constant during the regeneration, pretreatment and precipitation methods of the invention, the solution Eh value will tend to decrease. This decrease in Eh can move the solution outside of the MnO2 stability area, and result in oxides of manganese with diminished target loading rates and/or diminished valence states. Rather than maintaining pH constant, additional oxidizer could be required to maintain sufficient Eh levels as to remain within the MnO2 stability area. Figure 10, presents the pH and Eh values for precipitation reactions where: 1) the pH is controlled at a constant set point of 1.85 (Example1) for the duration of the reaction and 2) the pH is uncontrolled, or allow to exhibit a greater swing throughout the reaction. The resulting solution Eh value for the uncontrolled case is approximately 50 millivolts below the controlled case, but additionally the controlled case reached its stable Eh value at about 12 minutes where the uncontrolled case took about 19 minutes to reach its stable Eh value. One possible result of the decreased solution Eh and the loss of time at the stable Eh condition would be to move the solution outside of the MnO2 stability area, producing oxides of manganese with decreased target pollutant loading rates or to require additional reaction time, which could negatively affect the overall economics of the regeneration, pretreatment, or precipitation process. Applicants utilize their system for electronic process controls (discussed in this application) to avoid such negative impacts.

While exemplary embodiments of this invention and methods of practicing the same have been illustrated and described, it should be understood that various changes, adaptations, and modifications might be made therein without departing from the spirit of the invention and the scope of the appended claims.

What is claimed is:

1.   A method for rapid and adaptive recovery of metal values as precipitates of oxides of metals having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material, comprising:

                leaching metal values from ore or other metal oxide containing material to form a solution containing cations and anions of disassociated metal salts;

                heating the solution containing cations and anions of disassociated metal salts;

                mixing the heated solution containing cations and anions of disassociated metal salts and a heated aqueous oxidizing solution in a precipitation vessel to form a solution mixture, the heated aqueous oxidizing solution being prepared so as to have Eh and pH values within the metal oxide stability area of an aqueous solution heated to a temperature at or near boiling temperature at atmospheric pressure and being heated to a temperature at or near the boiling temperature;

                monitoring and adjusting the temperature, Eh value and pH value of the solution mixture so as to rapidly move mixture conditions into and to maintain them within the metal oxide stability area; and

                maintaining the solution conditions within the metal oxide stability area so as to precipitate the metal cations out of solution as precipitated oxides of metal having loading capacities and/or average oxidation states equal to or greater than that of the metal oxides in the ore or other raw material.

2.   A method for rapid and adaptive recovery of manganese values as precipitates of oxides of manganese having loading capacities and/or oxidation states equal to or greater than that of the oxides of manganese in the ore or other raw material, comprising:

                leaching manganese values from ore or other metal oxide containing material to form a solution containing cations and anions of disassociated manganese salts;

                heating the solution containing cations and anions of disassociated manganese salts;

                mixing the heated solution containing cations and anions of disassociated manganese salts and a heated aqueous oxidizing solution in a precipitation vessel to form a solution mixture, the heated aqueous oxidizing solution being prepared so as to have Eh and pH values within the MnO_2 stability area of an aqueous solution heated

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to a temperature at or near boiling temperature at atmospheric pressure and being heated to a temperature at or near the boiling temperature;

monitoring and adjusting the temperature, Eh value and pH value of the solution mixture so as to rapidly move mixture conditions into and to maintain them within the MnO2 stability area; and

maintaining the solution conditions within the MnO2 stability area so as to precipitate the manganese cations out of solution as precipitated oxides of manganese having loading capacities and/or average oxidation states equal to or greater than that of the oxides of manganese in the ore or other raw material.

3.   The method of any one of claims 1-2, further comprising the step:

maintaining solution or solution mixture pH constant throughout the processing cycle.

4.   The method of claim 1 further comprising the steps of :

separating the oxides of metal from the aqueous oxidizing solution to provide separated oxides of metal and a oxidation filtrate, the oxidation filtrate being routed for further processing and handling;

rinsing and filtering the separated oxides of metal to provide rinsed oxides of metal and a rinse filtrate, the rinse filtrate being directed for further handling and processing;

optionally, drying and/or comminuting the rinsed oxides of metal.

5.   The method of claim 2 further comprising the steps of :

separating the oxides of manganese from the aqueous oxidizing solution to provide separated oxides of manganese and a oxidation filtrate, the oxidation filtrate being routed for further processing and handling;

rinsing and filtering the separated oxides of manganese to provide rinsed oxides of manganese and a rinse filtrate, the rinse filtrate directed further handling and processing;

optionally, drying and/or comminuting the rinsed oxides of manganese.

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6.   The method of any one of claims 1-2, wherein the aqueous oxidizing solution contains an oxidant or oxidizer compatible with chemicals used to adjust the pH.

7.   The method of any one of claims 1-2, wherein the aqueous oxidizing solution contains an oxidant or oxidizer selected from the group consisting of persulfates, chlorates, perchlorates, permanganates, peroxides, hypochlorites, oxygen, air, and ozone (O3).

8.   The method of claim 1, wherein temperature, Eh and pH are maintained within the metal oxide stability area for a period ranging from about 20 to about 70 minutes.

9.   The method claim 2, wherein temperature, Eh and pH are maintained within the MnO2 stability area for a period ranging from about 20 to about 70 minutes.

10.   The method of claim 1, wherein temperature, Eh and pH are maintained within the metal oxide stability area for a period ranging from about 35 to about 55 minutes.

11.   The method of claim 2, wherein temperature, Eh and pH are maintained within the MnO2 stability area for a period ranging from about 35 to about 55 minutes.

12.   The method of claim 1, wherein temperature, Eh and pH are maintained within the metal oxide stability area for a period ranging from about 40 to about 50 minutes.

13.   The method of claim 2, wherein temperature, Eh and pH are maintained within the MnO2 stability area for a period ranging from about 40 to about 50 minutes.

14.   Oxides of metal produced by a method of rapid and adaptive recovery of metal values as precipitates of oxides of metals having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material, the method comprising the steps of:

        leaching metal values from ore or other metal oxide containing material to form a solution containing cations and anions of disassociated metal salts;

        heating the solution containing cations and anions of disassociated metal salts;

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mixing the heated solution containing cations and anions of disassociated metal salts and a heated aqueous oxidizing solution in a precipitation vessel to form a solution mixture, the heated aqueous oxidizing solution being prepared so as to have Eh and pH values within the metal oxide stability area of an aqueous solution heated to a temperature at or near boiling temperature at atmospheric pressure and being heated to a temperature at or near the boiling temperature;

monitoring and adjusting the temperature, Eh value and pH value of the solution mixture so as to rapidly move mixture conditions into and to maintain them within the metal oxide stability area; and

maintaining the solution conditions within the metal oxide stability area so as to precipitate the metal cations out of solution as precipitated oxides of metal having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material.

15.   Oxides of manganese produced by a method of rapid and adaptive recovery of manganese values as precipitates of oxides of manganese having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material, the method comprising:

leaching manganese values from ore or other raw material to form a solution containing cations and anions of disassociated manganese salts;

heating the solution containing cations and anions of disassociated manganese salts;

mixing the heated solution containing cations and anions of disassociated manganese salts and a heated aqueous oxidizing solution in a precipitation vessel to form a solution mixture, the heated aqueous oxidizing solution being prepared so as to have Eh and pH values within the MnO2 stability area of an aqueous solution heated to a temperature at or near boiling temperature at atmospheric pressure and being heated to a temperature at or near the boiling temperature;

monitoring and adjusting the temperature, Eh value and pH value of the solution mixture so as to rapidly move mixture conditions into and to maintain them within the MnO2 stability area; and

maintaining the solution conditions within the MnO2 stability area so as to precipitate the manganese cations out of solution as precipitated oxides of manganese

having loading capacities and/or oxidation states equal to or greater than that of the oxides of manganese in the ore or other raw material.

16.   The oxides of metal of claim 14, wherein the method further comprises the step of maintaining solution or solution mixture pH constant throughout the processing cycle.

17.   The oxides of manganese of claim 15, wherein the method further comprises the step of maintaining solution or solution mixture pH constant throughout the processing cycle.

18.   The oxides of metal of claim 14, wherein the method further comprises the steps of:

            separating the oxides of metal from the aqueous oxidizing solution to provide separated oxides of metal and a oxidation filtrate, the oxidation filtrate being routed for further processing and handling;

            rinsing and filtering the separated oxides of metal to provide rinsed oxides of metal and a rinse filtrate, the rinse filtrate being directed for further handling and processing; and

            optionally, drying and/or comminuting the rinsed oxides of metal.

19.   The oxides of manganese of claim 15, wherein the method further comprises the steps of:

            separating the oxides of manganese from the aqueous oxidizing solution to provide separated oxides of manganese and a oxidation filtrate, the oxidation filtrate being routed for further processing and handling;

            rinsing and filtering the separated oxides of manganese to provide rinsed oxides of manganese and a rinse filtrate, the rinse filtrate directed further handling and processing; and

            optionally, drying and/or comminuting the rinsed oxides of manganese.

20.   The oxides of metal of claim 14, wherein the aqueous oxidizing solution contains as oxidant or oxidizer selected from the group consisting of persulfates, chlorates, perchlorates, permanganates, peroxides, hypochlorites, oxygen, air, and ozone (O3).

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21.   The oxides of manganese of claim 15, wherein the aqueous oxidizing solution contains as oxidant or oxidizer selected from the group consisting of persulfates, chlorates, perchlorates, permanganates, peroxides, hypochlorites, oxygen, air, and ozone (O3).

5   22.   The oxides of metal of claim 14, wherein temperature, Eh and pH are maintained within the metal oxide stability area for a period ranging from about 20 to about 70 minutes.

23.   The oxides of manganese of claim 15, wherein temperature, Eh and pH are maintained within the MnO2 stability area for a period ranging from about 20 to about 70
10   minutes.

24.   The oxides of metal of claim 14, wherein temperature, Eh and pH are maintained within the metal oxide stability area for a period ranging from about 35 to about 55 minutes.

15   25.   The oxides of manganese of claim 15, wherein temperature, Eh and pH are maintained within the MnO2 stability area for a period ranging from about 35 to about 55 minutes.

26.   The oxides of metal of claim 14, wherein temperature, Eh and pH are maintained
20   within the metal oxide stability area for a period ranging from about 40 to about 50 minutes.

27.   The oxides of manganese of claim 15, wherein temperature, Eh and pH are maintained within the MnO2 stability area for a period ranging from about 40 to about 50 minutes.

25

28.   A system for rapid and adaptive recovery of metal values as precipitates of oxides of metal having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material, the system comprising:

        a well bore hole for injecting a leaching solution; a leaching solution injector;

30   a well bore hole for recovering a solution containing cations and anions of disassociated metal salts;

        solution recovering equipment; a precipitation vessel equipped with probes for measuring temperature, Eh and pH values of aqueous solutions within the

precipitation vessel, the precipitation vessel being configured for introduction of a solution containing cations and anions of disassociated metal salts;

a oxidant feeder containing a supply of aqueous oxidizing solution, the aqueous oxidizing solution being prepared so as to have Eh and pH values within the metal oxide stability area for an aqueous solution heated to a temperature at or near boiling temperature at atmospheric pressure;

a heater for providing heat to the precipitation vessel;

a base and/or acid feeder for feeding base or acid to the precipitation vessel;

at least one filtration and/or rinse unit, which optionally may be incorporated into and a part of the precipitation vessel; and

a controller for simultaneously monitoring and adjusting system operational parameters and regulating system components, the controller being in electronic communication with the probes of the precipitation vessel, the feeders, the at least one filtration and/or rinse unit and the heaters; the controller being capable of monitoring and adjusting system operational parameters selected from the group consisting of temperature, Eh, pH and feeder rates so as maintain conditions in the oxidation vessel within the metal oxide stability area through processing cycles.

29.   A system for rapid and adaptive recovery of manganese values as precipitates of oxides of manganese having loading capacities and/or oxidation states equal to or greater than that of the metal oxides in the ore or other raw material, the system comprising;

a well bore hole for injecting a leaching solution; a well bore hole for recovering a solution containing cations and anions of disassociated manganese salts;

solution recovering equipment; a leaching solution injector; a precipitation vessel equipped with probes for measuring temperature, Eh and pH values of aqueous solutions within the precipitation vessel, the precipitation vessel being configured for introduction of a solution containing cations and anions of disassociated manganese salts;

a oxidant feeder containing a supply of aqueous oxidizing solution, the aqueous oxidizing solution being prepared so as to have Eh and pH values within the MnO_2 stability area for an aqueous solution heated to a temperature at or near boiling temperature at atmospheric pressure;

a heater for providing heat to the precipitation vessel;

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a base and/or acid feeder for feeding base or acid to the precipitation vessel;

at least one filtration and/or rinse unit, which optionally may be incorporated into and a part of the precipitation vessel; and

a controller for simultaneously monitoring and adjusting system operational parameters and regulating system components, the controller being in electronic communication with the probes of the precipitation vessel, the feeders, the at least one filtration and/or rinse unit and the heaters; the controller being capable of monitoring and adjusting system operational parameters selected from the group consisting of temperature, Eh, pH and feeder rates so as maintain conditions in the oxidation vessel within the MnO_2 stability area through processing cycles.

FIGURE 1
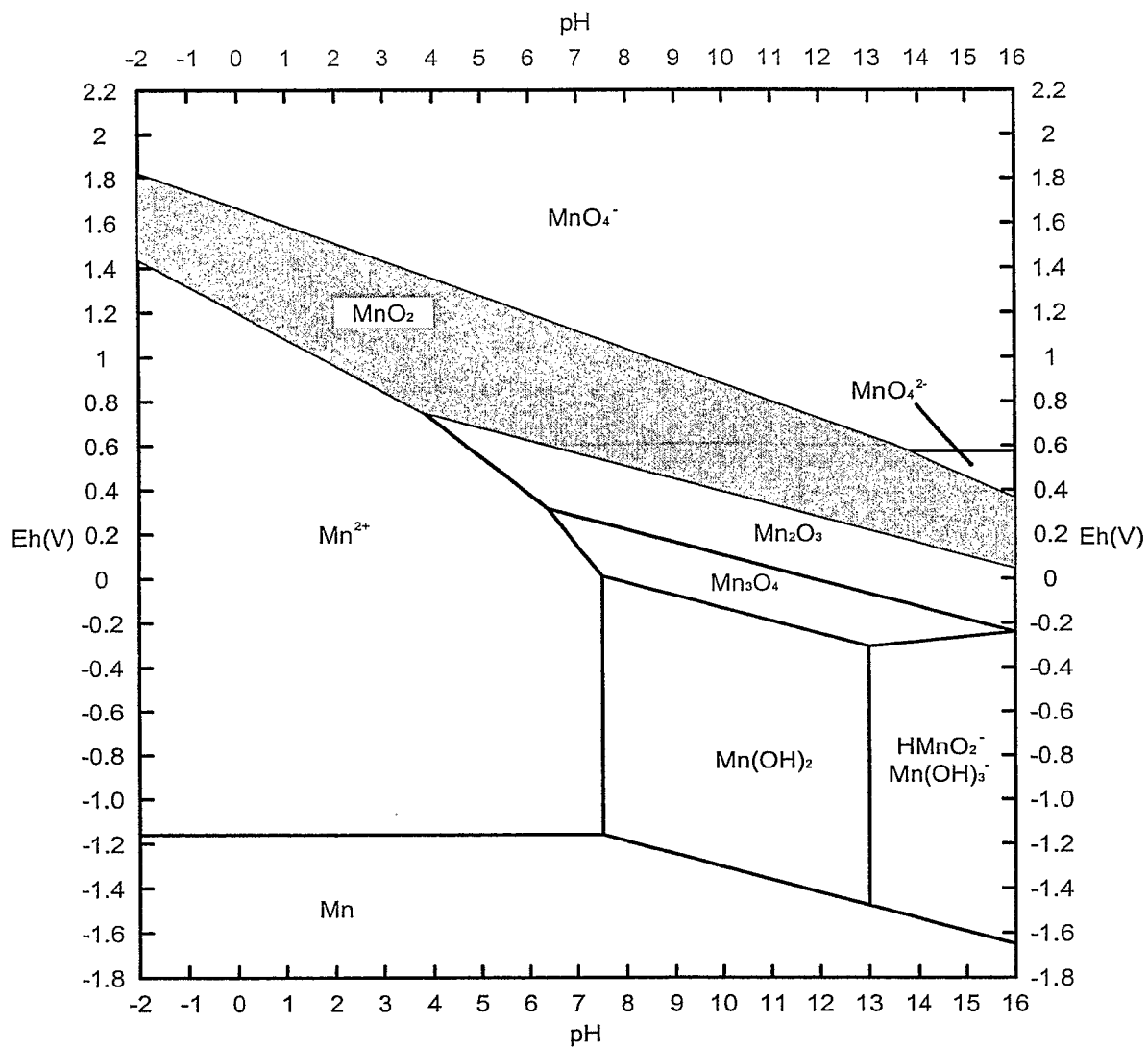POURBAIX DIAGRAM AT 25° C WITH 1×10^{0} DISSOLVED MANGANESE
CONCENTRATION

FIGURE 2
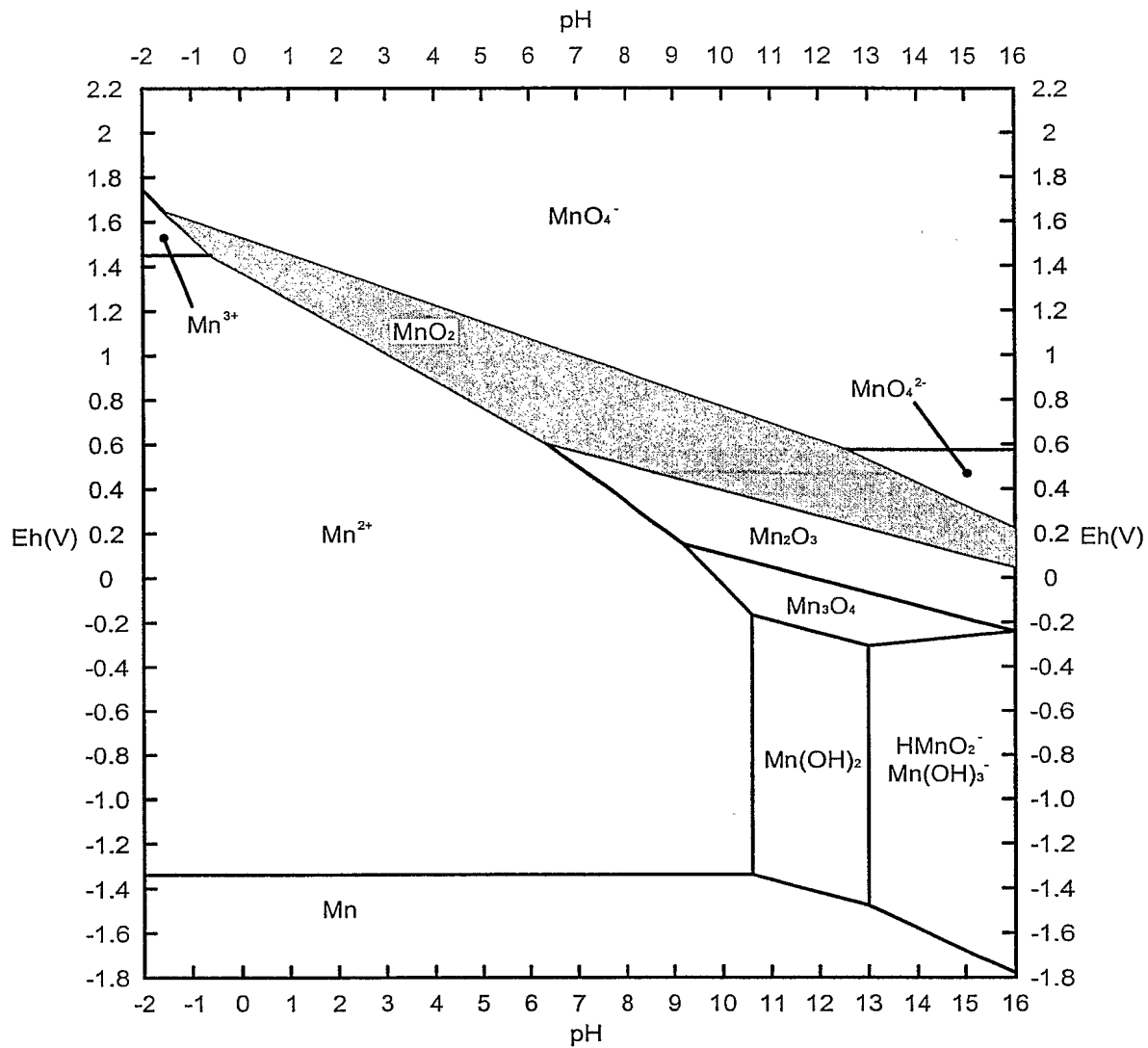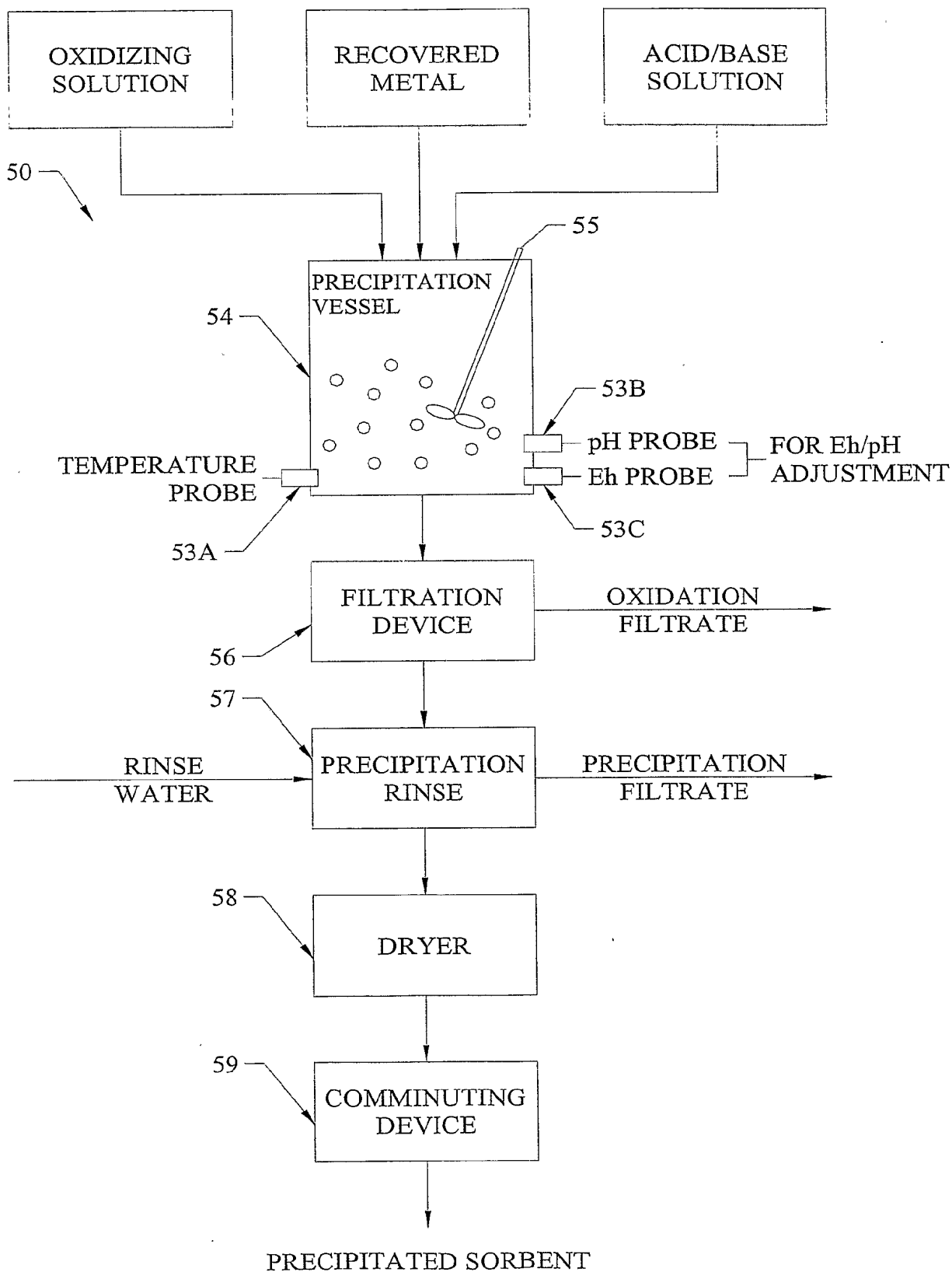POURBAIX DIAGRAM AT 25° C WITH 1x10⁻⁶ DISSOLVED MANGANESE
CONCENTRATION

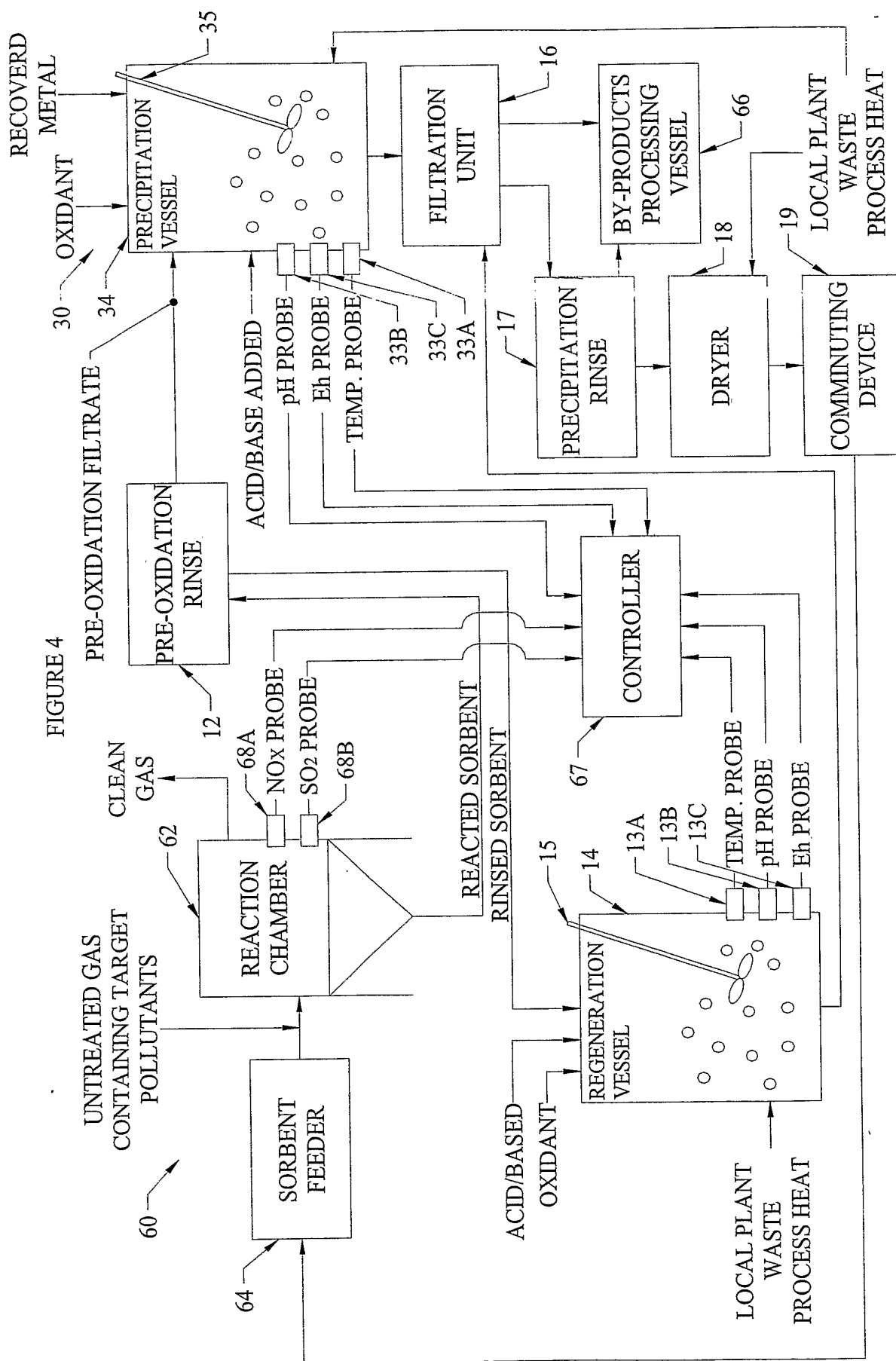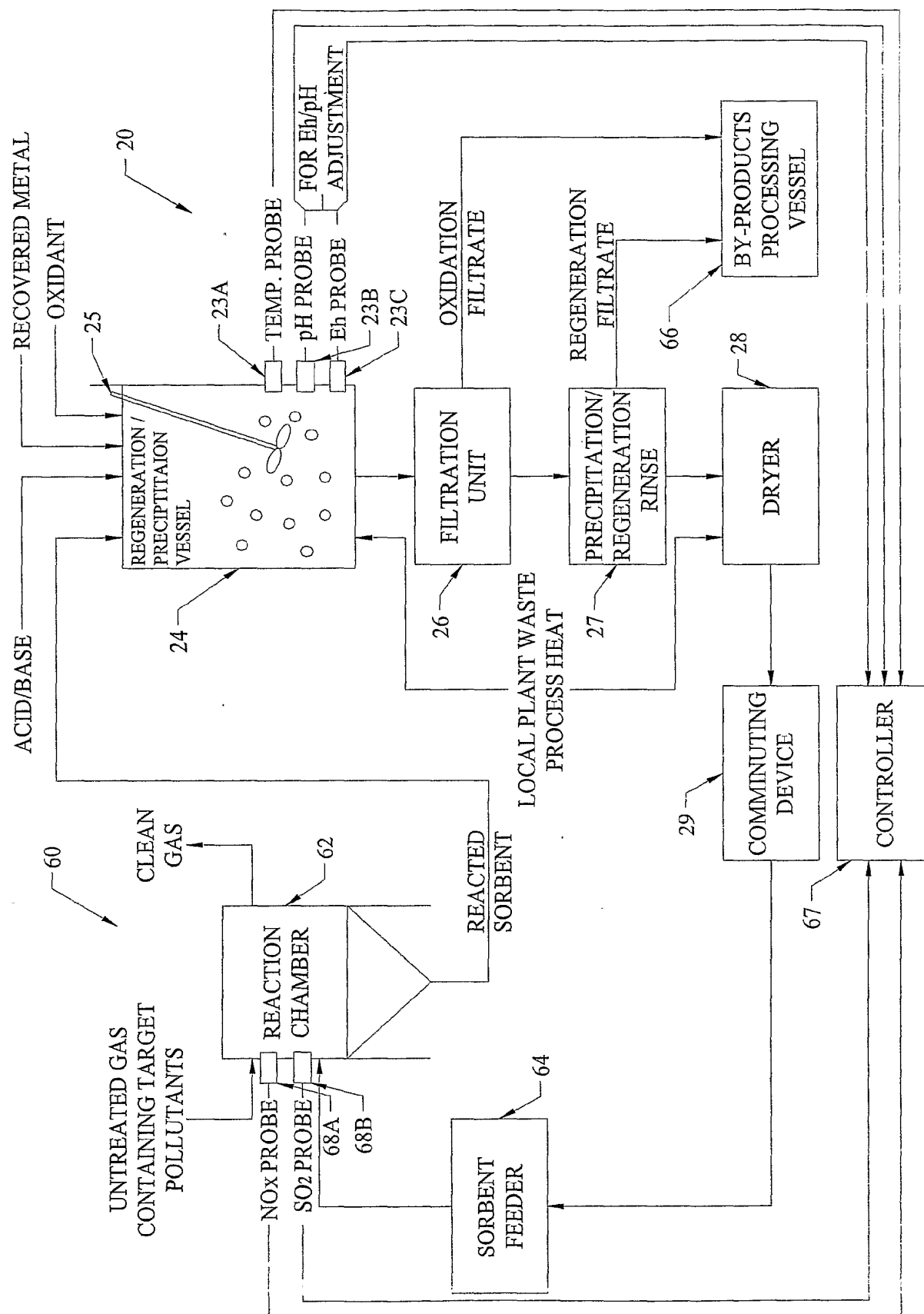FIGURE 3
PRECIPITATION OF VIRGIN OXIDES OF MANGANESE SORBENT

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

SO$_2$ Loading of Precipitated and Commercially Available Oxides of Manganese

Accumulative lbs of SO$_2$ Into the Test Reactor (multiplied by 1,000,000)

Accumulative lbs of SO$_2$ Out of the Test Reactor (multiplied by 1,000,000)

EMD   CMD   1.85 pH Precipitated (Example 1)   3.5 pH Precipitated (Example 2)

FIGURE 8

NOₓ Loading of Precipitated and Commercially Available Oxides of Manganese
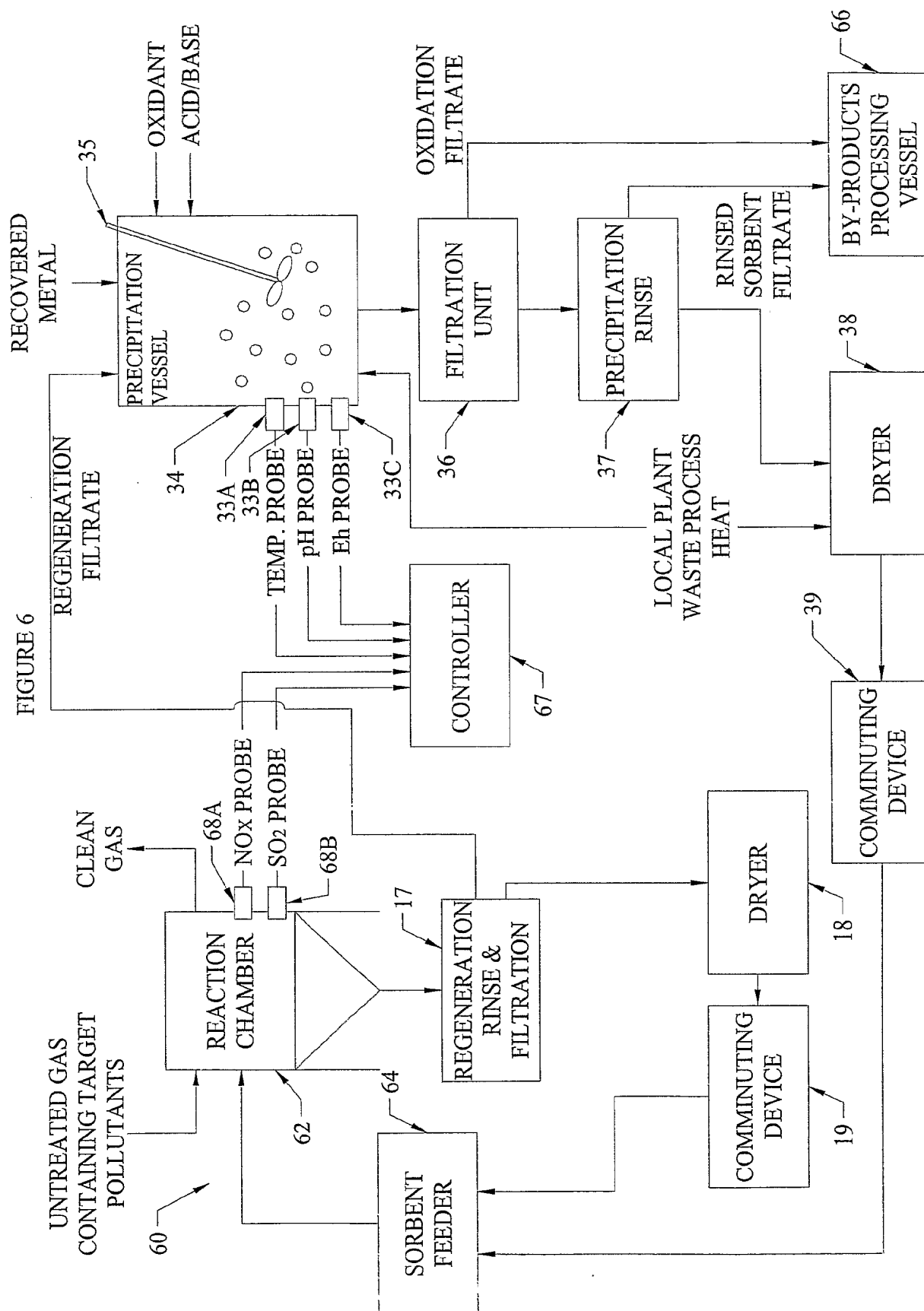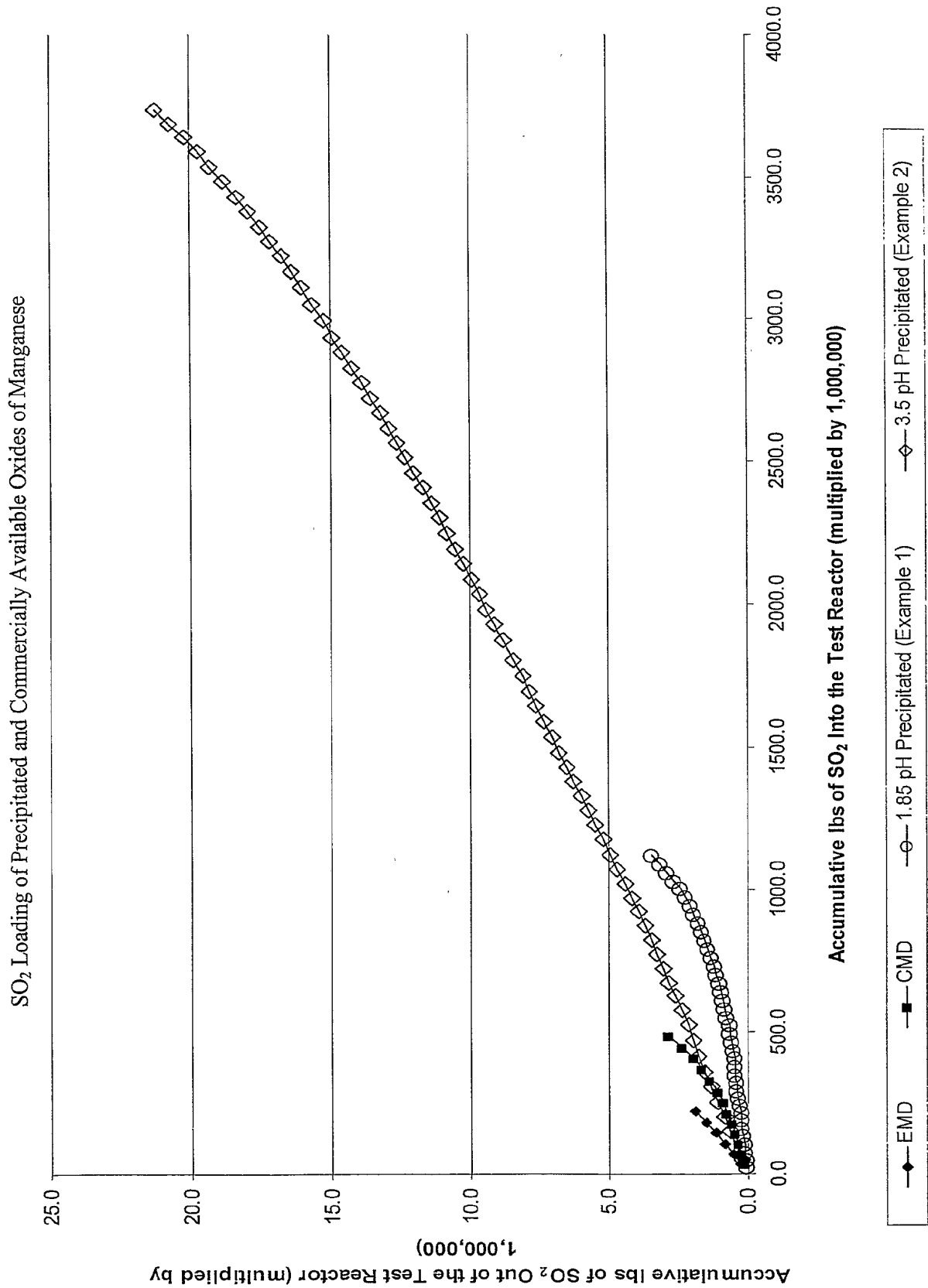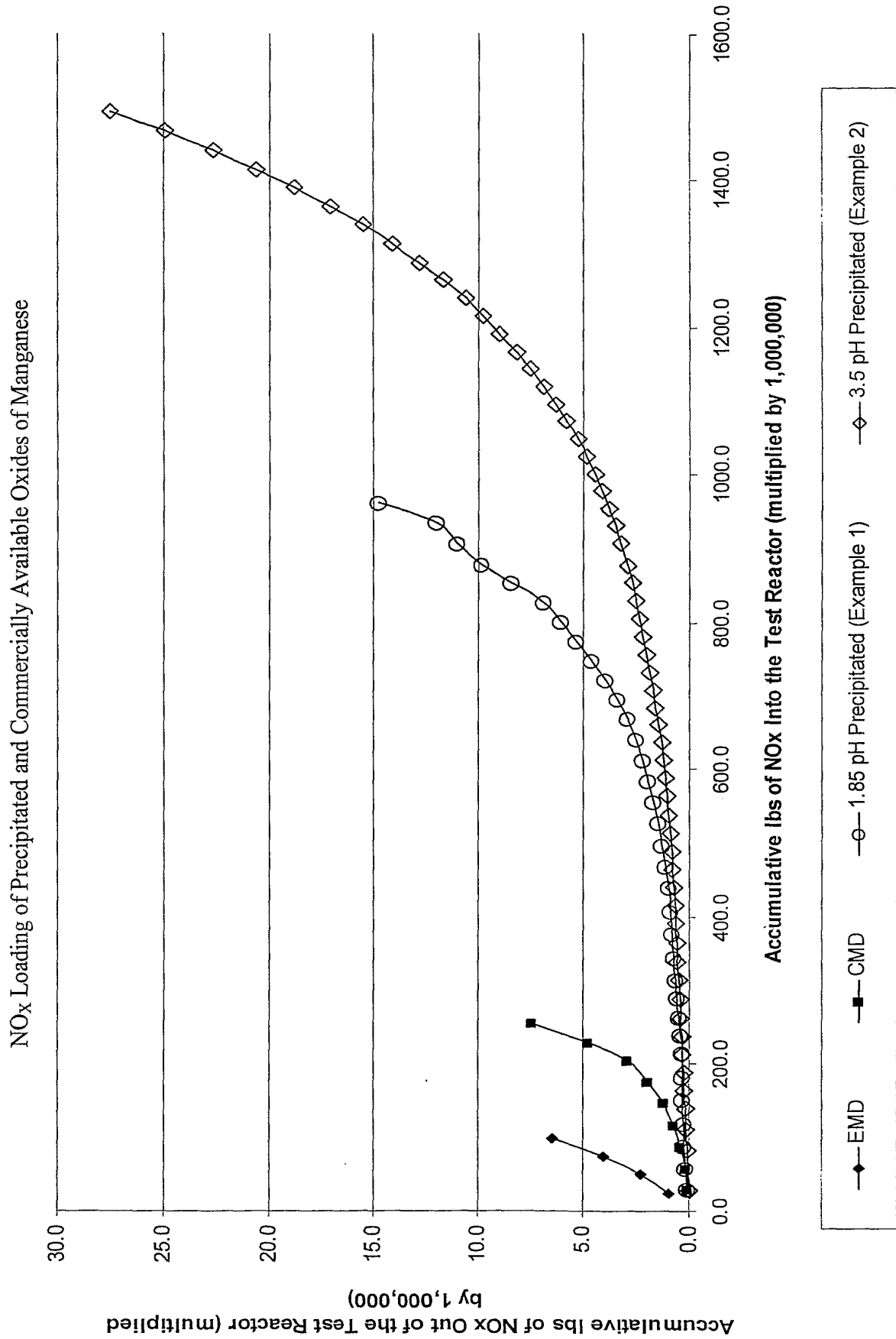
FIGURE 9

pH and Eh values for Oxides of Manganese Precipitation Examples 1 & 2

FIGURE 10

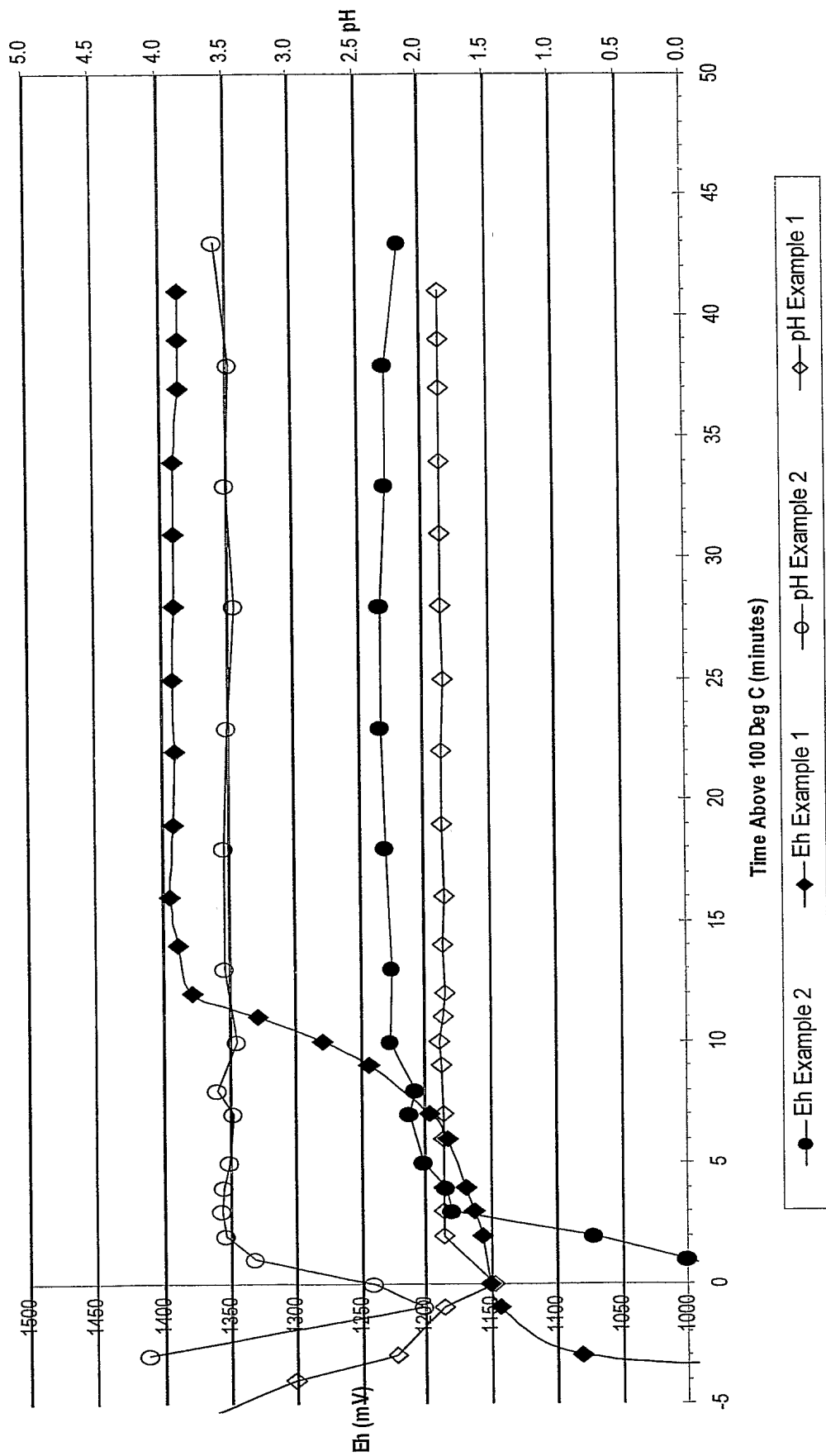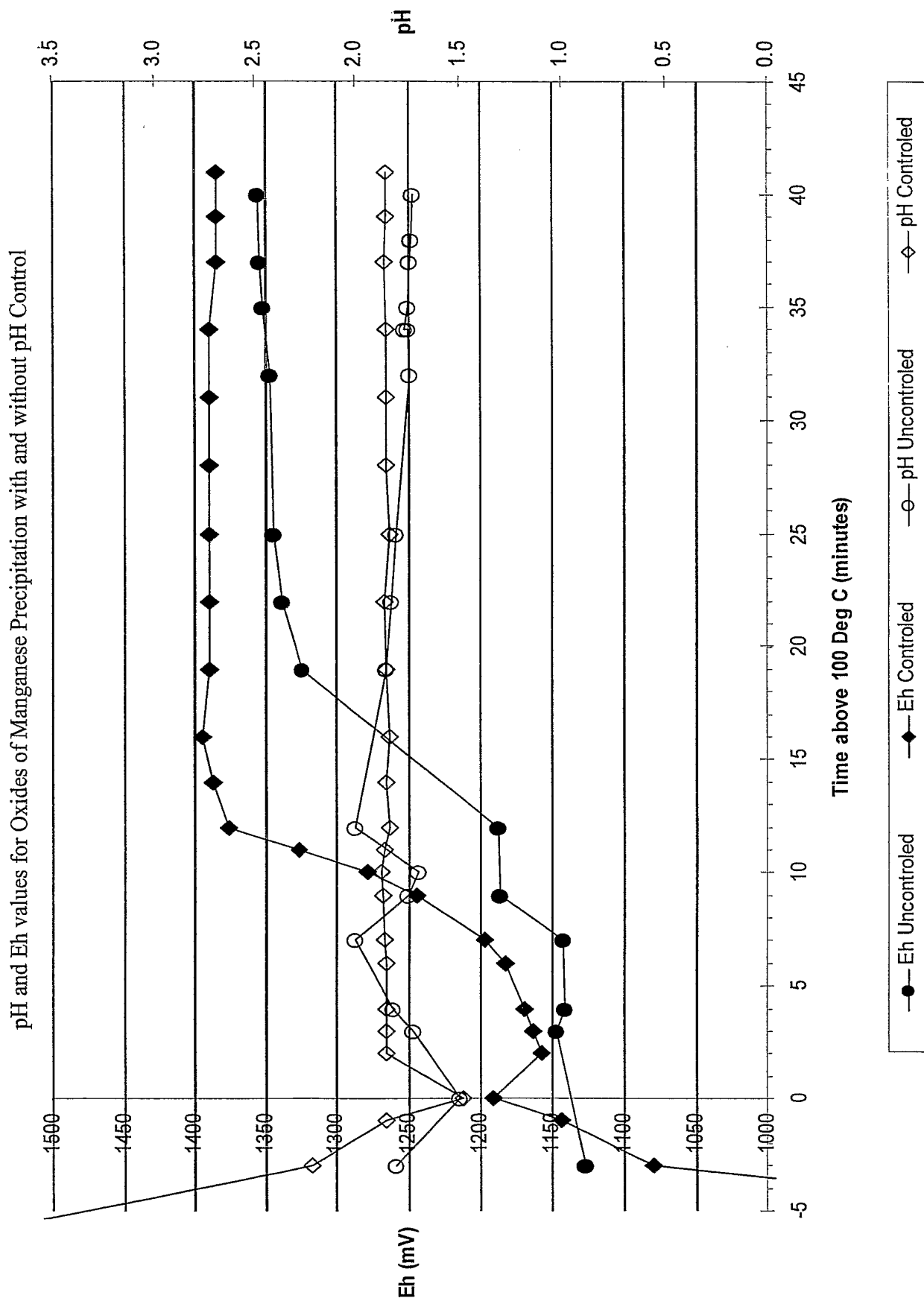pH and Eh values for Oxides of Manganese Precipitation with and without pH Control

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   B01J23/34   B01J20/00   C01G45/08   C22B47/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   B01J   C01G   C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 3 575 697 A (DOLEZAL HENRY) 20 April 1971 (1971-04-20) column 1, line 39 -column 2, line 52; claims; examples; tables ---	1-27
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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
14 October 2003	22/10/2003

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	US 4 276 268 A (WELSH JAY Y ET AL) 30 June 1981 (1981-06-30) column 1, line 62 -column 9, line 46; claims; figures; examples; tables	1-27
X	US 4 123 499 A (WELSH JAY Y ET AL) 31 October 1978 (1978-10-31) column 2, line 37 -column 6, line 45; claims; figures; examples; tables	1-27
X	EP 0 065 608 A (CHEMETALS CORP) 1 December 1982 (1982-12-01) page 3, line 2 -page 21, line 14; claims; figures; examples; tables	1-27
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INTERNATIONAL SEARCH REPORT

Ir   ation on patent family members

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